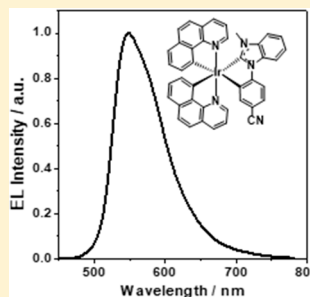


Neutral Cyclometalated Iridium(III) Complexes Bearing Substituted N-Heterocyclic Carbene (NHC) Ligands for High-Performance Yellow OLED Application

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S Supporting Information

ABSTRACT: The synthesis, crystal structure, and photophysics of a series of neutral cyclometalated iridium(III) complexes bearing substituted N-heterocyclic carbene (NHC) ancillary ligands ((C^N)₂Ir(R-NHC), where C^N and NHC refer to the cyclometalating ligand benzo[*h*]quinoline and 1-phenylbenzimidazole, respectively) are reported. The NHC ligands were substituted with electron-withdrawing or -donating groups on C4' of the phenyl ring (R = NO₂ (Ir1), CN (Ir2), OCH₃ (Ir4), N(CH₃)₂ (Ir5)) or C5 of the benzimidazole ring (R = NO₂ (Ir6), N(CH₃)₂ (Ir7)). The configuration of Ir1 was confirmed by a single-crystal X-ray diffraction analysis. The ground- and excited-state properties of Ir1–Ir7 were investigated by both spectroscopic methods and time-dependent density functional theory (TDDFT) calculations. All complexes possessed moderately strong structureless absorption bands at ca. 440 nm that originated from the C^N ligand based ¹π,π*/¹CT (charge transfer)/¹d,d transitions and very weak spin–forbidden ³MLCT (metal-to-ligand charge transfer)/³LLCT (ligand-to-ligand charge transfer) transitions beyond 500 nm. Electron-withdrawing substituents caused a slight blue shift of the ¹π,π*/¹CT/¹d,d band, while electron-donating substituents induced a red shift of this band in comparison to the unsubstituted complex Ir3. Except for the weakly emissive nitro-substituted complexes Ir1 and Ir6 that had much shorter lifetimes (≤160 ns), the other complexes are highly emissive in organic solutions with microsecond lifetimes at ca. 540–550 nm at room temperature, with the emitting states being predominantly assigned to ³π,π*/³MLCT states. Although the effect of the substituents on the emission energy was insignificant, the effects on the emission quantum yields and lifetimes were drastic. All complexes also exhibited broad triplet excited-state absorption at 460–700 nm with similar spectral features, indicating the similar parentage of the lowest triplet excited states. The highly emissive Ir2 was used as a dopant for organic light-emitting diode (OLED) fabrication. The device displayed a yellow emission with a maximum current efficiency (η_c) of 71.29 cd A^{−1}, a maximum luminance (L_{max}) of 32747 cd m^{−2}, and a maximum external quantum efficiency (EQE) of 20.6%. These results suggest the potential of utilizing this type of neutral Ir(III) complex as an efficient yellow phosphorescent emitter.



EQE: 20.6%
V_{on}: 2.9 V
L_{max}: 32747 cd/m²
η_c: 71.29 cd/A

Cathode: Al
EIL: LiF, 1 nm
ETL: TmPyPB, 55 nm
EML: CBP+10 wt% Ir2, 20 nm
EBL: TCTA, 5 nm
HTL: TAPC, 25 nm
HIL: HATCN, 5 nm
Anode: ITO

INTRODUCTION

Cyclometalated iridium(III) complexes have drawn tremendous attention in the past three decades due to their facile synthesis and intriguing photophysical characteristics.^{1,2} To date, cyclometalated Ir(III) complexes have been explored for various applications, such as organic light-emitting diodes (OLEDs),^{3,4} light-emitting electrochemical cells (LEECs),^{5–7} photodynamic therapy (PDT),^{8–10} nonlinear optics (NLO),^{11–16} and luminescent biological labeling.^{17,18} Due to the strong spin–orbit coupling effect induced by the Ir(III) ion, nearly quantitative triplet excited-state formation quantum yield and phosphorescence efficiency can be obtained in some

cases. Consequently, phosphorescent Ir(III) complexes appear promising as robust emissive dopants for OLED fabrication. In addition, the emission properties of the Ir(III) complexes can be readily tuned by modification of the cyclometalating and/or ancillary ligands because the characteristics of the emitting triplet excited state depends strongly on the nature of the ligands.

N-heterocyclic carbenes (NHCs), a type of strong σ-donating species, have been widely employed as ligands for

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organometallic complexes.^{19–29} Because of the strong ligand field strength of NHCs, the metal–carbene antibonding orbitals lead to a high-lying lowest unoccupied molecular orbital (LUMO) in the formed complexes and consequently the emission energy is blue-shifted and the emission quantum yield improved.^{20–24} To date, investigations on organoiridium complexes containing NHC ligands have been primarily aimed toward OLED applications.^{20–23} In the pioneering work reported by Thompson and co-workers,²⁰ two homoleptic neutral Ir(III) complexes with NHC ligands, i.e. *fac*-Ir(pmi)₃ (pmi = 1-phenyl-3-methylimidazolin-2-ylidene-*C*,*C*′) and *fac*-Ir(pmb)₃ (pmb = 1-phenyl-3-methylbenzimidazolin-2-ylidene-*C*,*C*′), showed higher emission energies but decreased photoluminescence (PL) efficiencies in comparison to the greenish emissive *fac*-Ir(ppy)₃ (ppy = 2-phenylpyridyl) and the sky blue emissive *fac*-Ir(F₂ppy)₃ (F₂ppy = 2-(2,4-difluorophenyl)pyridine) complexes. By replacing one NHC ligand with a diimine ligand, Kessler's group reported several cationic Ir(N[^]N)(NHC)₂⁺ complexes with yellow emission in neat films with PL efficiencies of up to 0.83.²⁵

The seminal work on the development of heteroleptic (C[^]N)₂Ir(NHC) type of complexes was reported by Bielawski and co-workers, in which one NHC ligand and two cyclometalating 2-phenylpyridyl (C[^]N) ligands were employed.²⁷ This complex emitted at 497 nm in MeTHF with an emission yield of 19%. More recently, Zuo and co-workers²² reported a series of heteroleptic neutral (C[^]N)₂Ir(NHC) complexes with various cyclometalating C[^]N and NHCs as the ligands. Among them, in the complexes with 2-(2,4-difluorophenyl)pyridine (dfppy) as the cyclometalating C[^]N ligand and NHCs bearing electron-withdrawing –F or –CF₃ substituents on the phenyl ring or NHCs with the phenyl ring being replaced with pyridine or pyrimidine rings, the emission was shifted to a bluer region. The blue-emitting OLED device utilizing (dfppy)₂Ir(CF₃-pmi) (CF₃-pmi = 1-(3-trifluoromethylphenyl)-3-methylimidazole) as the dopant gave a maximum current efficiency of 37.83 cd A^{–1}, an external quantum efficiency of 10.3%, and a maximum luminance of 8709 cd m^{–2}.

Although the obstacles of synthesis have been solved, further exploration of the (C[^]N)₂Ir(NHC)-type Ir(III) complexes remains dormant. Because of the promising applications of these types of complexes in OLEDs, we designed and synthesized seven (C[^]N)₂Ir(NHC)-type Ir(III) complexes (**Ir1**–**Ir7**, Chart 1) with different electron-donating (–OCH₃ or –N(CH₃)₂) or -withdrawing (–NO₂ or –CN) substituents on C5 of the benzimidazole or C4′ of the phenyl rings at the NHC ligand (i.e., 3-methyl-1-(4-nitrophenyl)benzimidazol-3-ium iodide (**L1**), 1-(4-cyanophenyl)-3-methylbenzimidazol-3-

ium iodide (**L2**), 3-methyl-1-phenylbenzimidazol-3-ium iodide (**L3**), 1-(4-methoxyphenyl)-3-methylbenzimidazol-3-ium iodide (**L4**), 1-(4-dimethylaminophenyl)-3-methylbenzimidazol-3-ium iodide (**L5**), 5-nitro-3-methyl-1-phenylbenzimidazol-3-ium iodide (**L6**), and 5-dimethylamino-3-methyl-1-phenylbenzimidazol-3-ium iodide (**L7**)) and benzo[*h*]quinoline as the C[^]N ligand. Selection of benzo[*h*]quinoline as the C[^]N ligand was due to its rigidity that may potentially reduce the nonradiative decay rates. Different electron-donating or -withdrawing substituents were introduced to the NHC ligand in order to understand the effect of the substituents at the NHC ligand on the photophysics of these (C[^]N)₂Ir(NHC)-type complexes. The structure of **Ir1** was determined by X-ray crystallography to confirm the configuration of these types of Ir(III) complexes.

EXPERIMENTAL SECTION

Synthesis and Characterizations. All chemicals and solvents were obtained from commercial sources and used as received without further purification. Silica gels (60 Å, 230–400 mesh) for column chromatography were purchased from Sorbent Technology. The precursor compounds **1** (1-(4-nitrophenyl)benzimidazole),³⁰ **2** (1-(4-cyanophenyl)benzimidazole),³¹ **3** (1-phenylbenzimidazole),³⁰ and **4** (1-(4-methoxyphenyl)benzimidazole)³⁰ were prepared according to the reported procedures (see Scheme 1 for the synthetic route). The C[^]N ligand benzo[*h*]quinoline was purchased from Alfa-Aesar, and its Ir dimer [Ir(benzo[*h*]quinoline)₂(μ-Cl)₂] was prepared by following the reported method.³² The synthetic schemes for the Ir(III) complexes **Ir1**–**Ir7** are provided in Scheme 1. The synthetic details for the precursor compounds **5**–**7**, the ligands **L1**–**L7**, and the complexes **Ir1**–**Ir7**, as well as the characterization data, are reported below.

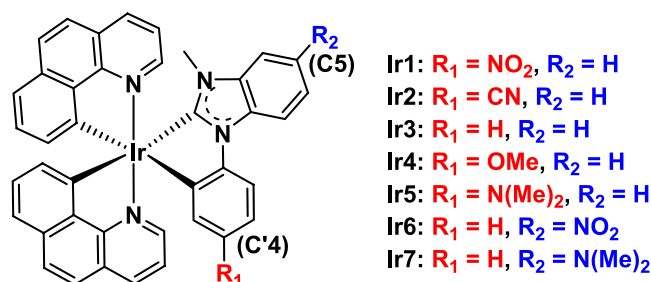
The structures of the ligands **L1**–**L7** were characterized by ¹H NMR spectroscopy, and the complexes **Ir1**–**Ir7** were characterized by ¹H NMR, electrospray ionization mass spectrometry (ESI–HRMS), and elemental analyses. In addition, the configuration of complex **Ir1** was determined by single-crystal X-ray crystallography. The ¹H NMR spectra were recorded on a Varian Oxford-400/Bruker-400 spectrometer in deuterated solvents (i.e. CDCl₃ or DMSO-*d*₆) using tetramethylsilane (TMS) as the internal standard. A Waters Synapt G2-Si mass spectrometer was used for the mass analyses. Elemental analyses were carried out by NuMega Resonance Laboratories, Inc. in San Diego, CA, USA. A Kappa Apex II Duo X-ray diffractometer was used to collect the X-ray diffraction (XRD) pattern of complex **Ir1**.

1-(4-Dimethylaminophenyl)benzimidazole (Compound **5**)

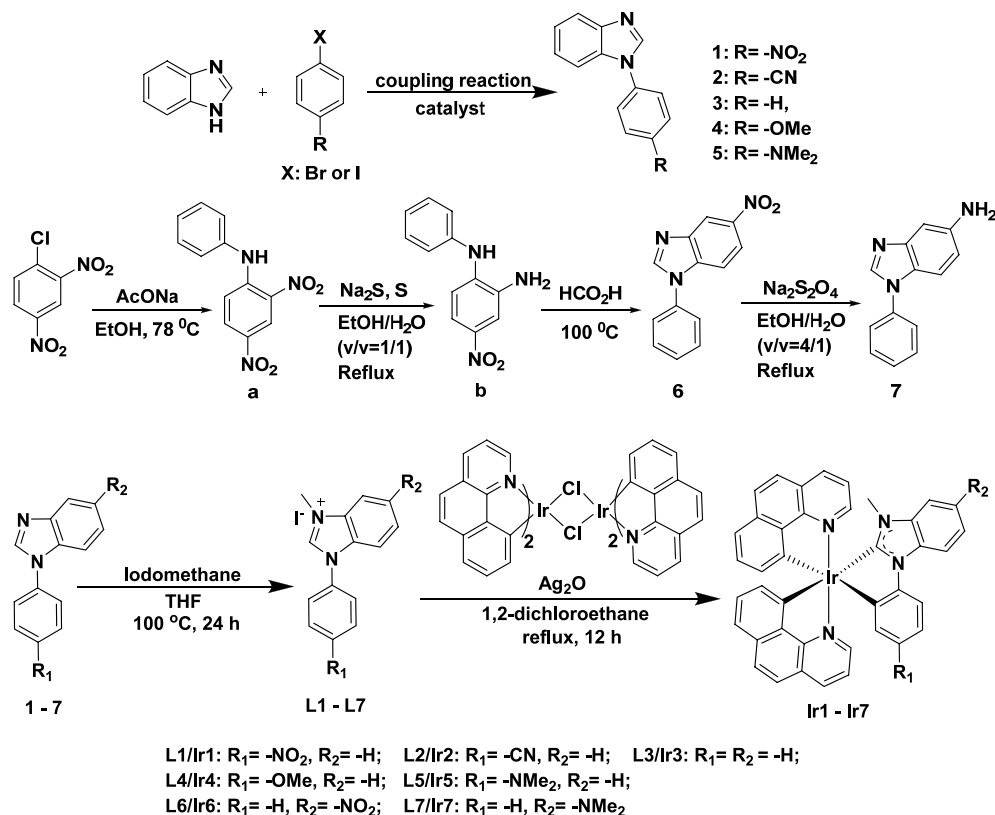
In a two-neck flask, 4-bromo-*N,N*-dimethylbenzenamine (2.00 g, 10 mmol), benzimidazole (1.18 g, 10 mmol), CuI (318 mg, 1.67 mmol), *L*-proline (383 mg, 3.33 mmol), and K₂CO₃ (2.76 g, 20 mmol) were mixed in 15 mL of DMSO and degassed with nitrogen for 30 min. The resulting mixture was heated to 130 °C for 24 h before it was partitioned between water and ethyl acetate. The organic layer was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The crude product was then loaded on a silica gel column and eluted with ethyl acetate/hexane (v/v 1/1) to afford the product as a yellow solid (960 mg, 40%). ¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H), 7.86 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.45 (dd, *J* = 5.9, 3.3 Hz, 1H), 7.38–7.27 (m, 4H), 6.85 (d, *J* = 3.4 Hz, 1H), 6.82 (d, *J* = 3.3 Hz, 1H), 3.04 (s, 6H).

2,4-Dinitro-*N*-phenylbenzenamine (Compound **a).** A mixture of 2,4-dinitrochlorobenzene (4.05 g, 20 mmol), aniline (2.05 g, 22 mmol), and sodium acetate (1.64 g, 20 mmol) was dissolved in ethanol (10 mL) and heated to reflux for 1 h. After the mixture was cooled to room temperature, the precipitated red-orange crystals were filtered out, washed with ethanol twice (10 mL each), and dried in vacuo to afford compound **a** as a red solid (4.70 g, 91%). ¹H NMR (500 MHz, CDCl₃): δ 9.98 (br, 1H), 9.19 (d, *J* = 2.6 Hz, 1H), 8.17 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 9.5 Hz, 1H).

Chart 1. Chemical Structures of (C[^]N)₂Ir(NHC) Complexes **Ir1–**Ir7****



Scheme 1. Synthetic Routes for Complexes Ir1–Ir7



4-Nitro-*N*¹-phenyl-1,2-benzenediamine (Compound b). A suspension of compound a (4.70 g, 18.1 mmol) in alcohol (30 mL) was added to a solution of Na₂S (2.82 g, 36.2 mmol) and sulfur powder (1.15 g, 36.2 mmol) in water (30 mL). The mixture was heated to reflux for 2 h, diluted with water (30 mL), and cooled to room temperature. The obtained precipitate was filtered out and washed with warm water to give dark brown crystals of the title compound (4.10 g, 99%). ¹H NMR (400 MHz, CDCl₃): δ 7.77–7.64 (m, 2H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 8.9 Hz, 1H), 7.12–6.97 (m, 3H), 5.76 (br, 1H), 3.70 (br, 2H).

5-Nitro-1-phenylbenzimidazole (Compound 6). A mixture of compound b (687 mg, 3 mmol) and formic acid (50 mL) was stirred at 100 °C for 12 h. Then, the reaction mixture was cooled to room temperature and concentrated in vacuo to afford a solid. The crude solid was partitioned between ethyl acetate (250 mL) and 30% ammonium hydroxide (25 mL). The organic layer was collected and concentrated in vacuo to afford compound 6 as an orange solid (710 mg, 99%). ¹H NMR (400 MHz, CDCl₃): δ 8.83 (d, *J* = 2.1 Hz, 1H), 8.33–8.26 (m, 2H), 7.67 (t, *J* = 7.7 Hz, 2H), 7.63–7.57 (m, 2H), 7.57–7.51 (m, 2H).

1-Phenylbenzimidazol-5-amine (Compound 7). Compound 6 (239 mg, 1 mmol) was dissolved in 10 mL of ethanol/water (v/v 4/1). Then, sodium dithionite (1.74 g, 10 mmol) was added to the solution and the resulting mixture was heated to reflux for 4 h. The reaction mixture was diluted with ethyl acetate and washed with water. The water layer was extracted several times with ethyl acetate. The organic layers were combined, dried over sodium sulfate, and concentrated to yield compound 7 as a white solid (200 mg, 96%). ¹H NMR (400 MHz, CDCl₃): δ 8.02 (s, 1H), 7.61–7.52 (m, 2H), 7.50 (t, *J* = 4.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 6.76 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.35 (br, 2H).

General Synthetic Procedure for Ligands L1–L7. A mixture of 1 mmol of the corresponding precursor (compounds 1–7), 1.5 mmol of iodomethane (3 mmol for L7), and 10 mL of tetrahydrofuran was placed in a pressure tube with a Teflon cap and heated to 100 °C for 24 h. After the mixture was cooled to room

temperature, the resulting solid was filtered out, washed with tetrahydrofuran, and dried in vacuo.

L1. A white solid was obtained as the target compound (358 mg, 94%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.25 (s, 1H), 8.60 (d, *J* = 9.2 Hz, 2H), 8.18 (d, *J* = 7.6 Hz, 1H), 8.13 (d, *J* = 9.1 Hz, 2H), 7.97–7.90 (m, 1H), 7.85–7.68 (m, 2H), 4.20 (s, 3H).

L2. A white solid was obtained as the target compound (336 mg, 93%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.19 (d, *J* = 0.6 Hz, 1H), 8.33–8.23 (m, 2H), 8.21–8.12 (m, 1H), 8.05 (d, *J* = 8.5 Hz, 2H), 7.92 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.84–7.67 (m, 2H), 4.18 (s, 3H).

L3. A white solid was obtained as the target compound (218 mg, 65%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.12 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.87–7.68 (m, 8H), 4.17 (s, 3H).

L4. A white solid was obtained as the target compound (245 mg, 67%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.02 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.80–7.66 (m, 5H), 7.28 (d, *J* = 8.9 Hz, 2H), 4.16 (s, 3H), 3.89 (s, 3H).

L5. A white solid was obtained as the target compound (349 mg, 92%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.95 (s, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.82–7.64 (m, 3H), 7.56 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 4.14 (s, 3H), 3.03 (s, 6H).

L6. A yellow solid was obtained as the target compound (127 mg, 33%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.40 (s, 1H), 9.21 (d, *J* = 2.1 Hz, 1H), 8.52 (dd, *J* = 9.2, 2.1 Hz, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.86–7.73 (m, 5H), 4.28 (s, 3H).

L7. A white solid was obtained as the target compound (281 mg, 71%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.83 (s, 1H), 7.80–7.68 (m, 5H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.16 (dd, *J* = 9.3, 2.2 Hz, 1H), 7.12 (d, *J* = 2.1 Hz, 1H), 4.07 (s, 3H), 3.06 (s, 6H).

General Synthetic Procedure for Complexes Ir1–Ir7. The corresponding ligand L1–L7 (0.06 mmol), [Ir(benzo[*h*]quinoline)₂(μ-Cl)₂] (35 mg, 0.03 mmol), and Ag₂O (28 mg, 0.12 mmol) were dissolved in 10 mL of 1,2-dichloroethane, and the reaction mixture was heated to reflux in the dark for 12 h (1 h for Ir6). The solution was then cooled to room temperature. After removal of the solvent under reduced pressure, purification by silica

gel column chromatography with dichloromethane and hexane (v/v 1/1) as eluent afforded a yellow solid as the target complex.

Ir1: 40 mg (yield: 83%). ^1H NMR (400 MHz, CDCl_3): δ 8.29 (d, J = 5.4 Hz, 1H), 8.24 (d, J = 5.4 Hz, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.96–7.87 (m, 2H), 7.80 (d, J = 6.4 Hz, 1H), 7.78 (d, J = 6.4 Hz, 1H), 7.62–7.48 (m, 3H), 7.46–7.39 (m, 2H), 7.38–7.31 (m, 2H), 7.28 (s, 1H), 7.24–7.04 (m, 4H), 6.71 (d, J = 6.8 Hz, 1H), 6.35 (d, J = 7.1 Hz, 1H), 3.28 (s, 3H). ESI-HRMS (m/z): calcd for $[\text{C}_{40}\text{H}_{26}\text{N}_5\text{O}_3\text{Ir} + \text{H}]^+$, 802.1796; found, 802.1772. Anal. Calcd for $\text{C}_{40}\text{H}_{26}\text{N}_5\text{O}_3\text{Ir}$: C, 59.99; H, 3.27; N, 8.74. Found: C, 59.96; H, 3.62; N, 8.73.

Ir2: 26 mg (yield: 56%). ^1H NMR (400 MHz, CDCl_3): δ 8.28 (d, J = 5.4 Hz, 1H), 8.26 (d, J = 5.5 Hz, 1H), 8.19 (d, J = 7.7 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.1 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.59 (d, J = 5.3 Hz, 1H), 7.56 (d, J = 5.2 Hz, 1H), 7.49–7.31 (m, 5H), 7.29 (s, 1H), 7.24–7.03 (m, 5H), 6.72 (d, J = 6.9 Hz, 1H), 6.32 (d, J = 7.1 Hz, 1H), 3.30 (s, 3H). ESI-HRMS (m/z): calcd for $[\text{C}_{41}\text{H}_{26}\text{N}_5\text{Ir} + \text{H}]^+$, 782.1897; found, 782.1872. Anal. Calcd for $\text{C}_{41}\text{H}_{26}\text{N}_5\text{Ir}$: C, 63.06; H, 3.36; N, 8.97. Found: C, 63.32; H, 3.75; N, 8.89.

Ir3: 9 mg (yield: 20%). ^1H NMR (400 MHz, CDCl_3): δ 8.36 (d, J = 4.5 Hz, 1H), 8.30 (d, J = 4.7 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.04 (d, J = 7.8 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.40–7.31 (m, 3H), 7.28 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.17–7.00 (m, 5H), 6.81 (d, J = 5.7 Hz, 1H), 6.74 (t, J = 6.2 Hz, 2H), 6.37 (d, J = 7.0 Hz, 1H), 3.27 (s, 3H). ESI-HRMS (m/z): calcd for $[\text{C}_{40}\text{H}_{27}\text{N}_4\text{Ir} + \text{H}]^+$, 757.1945; found, 757.1938. Anal. Calcd for $\text{C}_{40}\text{H}_{27}\text{N}_4\text{Ir} \cdot 0.1\text{CH}_2\text{Cl}_2$: C, 63.01; H, 3.59; N, 7.33. Found: C, 62.77; H, 3.30; N, 7.26.

Ir4: 10 mg (yield: 4%) (by scaling up all of the reagents and solvent to 5-fold of the scale described in the above general synthetic procedure). ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, J = 4.9 Hz, 1H), 8.30 (d, J = 5.7 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 7.1 Hz, 1H), 8.00 (d, J = 7.4 Hz, 1H), 7.80 (d, J = 8.7 Hz, 1H), 7.76 (d, J = 3.0 Hz, 1H), 7.74 (d, J = 3.2 Hz, 1H), 7.53 (d, J = 8.9 Hz, 1H), 7.50 (d, J = 8.7 Hz, 1H), 7.40–7.30 (m, 3H), 7.25–6.95 (m, 6H), 6.75 (d, J = 6.8 Hz, 1H), 6.55 (dd, J = 8.6, 2.9 Hz, 1H), 6.40 (d, J = 3.0 Hz, 1H), 6.37 (d, J = 7.0 Hz, 1H), 3.48 (s, 3H), 3.25 (s, 3H). ESI-HRMS (m/z): calcd for $[\text{C}_{41}\text{H}_{29}\text{N}_4\text{OIr} + \text{H}]^+$, 787.2051; found, 787.2041. Anal. Calcd. for $\text{C}_{41}\text{H}_{29}\text{N}_4\text{OIr} \cdot 0.2\text{CH}_2\text{Cl}_2 \cdot 0.1\text{C}_6\text{H}_{14}$ (C_6H_{14} = hexane): C, 61.87; H, 3.83; N, 6.90. Found: C, 62.10; H, 3.67; N, 6.51.

Ir5: 10 mg (yield: 4%) (by scaling up all of the reagents and solvent to 5-fold of the scale described in the above general synthetic procedure). ^1H NMR (400 MHz, CDCl_3): δ 8.44 (d, J = 4.4 Hz, 1H), 8.32 (d, J = 5.5 Hz, 1H), 8.15 (d, J = 8.1 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.98 (d, J = 7.3 Hz, 1H), 7.82–7.70 (m, 3H), 7.53 (d, J = 8.8 Hz, 1H), 7.49 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 7.9 Hz, 3H), 7.22 (d, J = 6.6 Hz, 2H), 7.17–7.09 (m, 3H), 7.06 (dd, J = 8.0, 5.4 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 6.49–6.36 (m, 2H), 6.32 (d, J = 2.9 Hz, 1H), 3.25 (s, 3H), 2.55 (s, 6H). ESI-HRMS (m/z): calcd for $[\text{C}_{42}\text{H}_{32}\text{N}_5\text{Ir} + \text{H}]^+$, 800.2367; found, 800.2333. Anal. Calcd for $\text{C}_{42}\text{H}_{32}\text{N}_5\text{Ir} \cdot 0.1\text{CH}_2\text{Cl}_2$: C, 62.62; H, 4.02; N, 8.67. Found: C, 62.59; H, 3.85; N, 9.05.

Ir6: 23 mg (yield: 48%). ^1H NMR (400 MHz, CDCl_3): δ 8.48–8.22 (m, 4H), 8.19 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.81 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.41 (t, J = 8.2 Hz, 2H), 7.25–7.02 (m, 5H), 6.91–6.79 (m, 2H), 6.76 (d, J = 6.9 Hz, 1H), 6.33 (d, J = 6.8 Hz, 1H), 3.39 (s, 3H). ESI-HRMS (m/z): calcd for $[\text{C}_{40}\text{H}_{26}\text{N}_5\text{O}_2\text{Ir} + \text{H}]^+$, 802.1796; found, 802.1785. Anal. Calcd. for $\text{C}_{40}\text{H}_{26}\text{N}_5\text{O}_2\text{Ir} \cdot 0.1\text{C}_6\text{H}_{14} \cdot 3\text{H}_2\text{O}$: C, 56.47; H, 3.90; N, 8.11. Found: C, 56.38; H, 4.20; N, 8.06.

Ir7: 19 mg (yield: 40%). ^1H NMR (400 MHz, CDCl_3): δ 8.39 (d, J = 5.4 Hz, 1H), 8.36 (d, J = 5.3 Hz, 1H), 8.07–8.00 (m, 2H), 7.83 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.8 Hz, 1H), 7.23–6.99 (m, 6H), 6.89–6.72 (m, 4H), 6.47 (d, J = 2.1 Hz, 1H), 6.41 (d, J = 7.0 Hz, 1H), 3.22 (s, 3H), 3.00 (s, 6H). ESI-HRMS

(m/z): calcd for $[\text{C}_{42}\text{H}_{32}\text{N}_5\text{Ir} + \text{H}]^+$, 800.2367; found, 800.2357. Anal. Calcd for $\text{C}_{42}\text{H}_{32}\text{N}_5\text{Ir} \cdot 0.9\text{C}_6\text{H}_{14} \cdot 4\text{H}_2\text{O}$: C, 60.02; H, 5.59; N, 7.38. Found: C, 59.89; H, 5.98; N, 7.76.

Photophysical Studies. The solvents used for the photophysical studies are spectrophotometric grade and were purchased from Alfa Aesar Co., Inc. The ultraviolet–visible (UV–vis) absorption spectra of Ir1–Ir7 were recorded on a Varian Cary 50 spectrophotometer. The steady-state emission spectra of Ir1–Ir7 were collected on a HORIBA FluoroMax 4 fluorometer/phosphorometer. The absolute emission quantum yields (Φ_{em}) were determined via a fiber coupled Ocean Optics integrating sphere. A broad white light LED was used as the excitation light source, which was connected to a set of Delta linear-variable filters (LVFs) and then to the integrating sphere via a fiber. The excitation wavelength was narrowed and positioned at 450 nm using the LVFs. Ocean Optics UV–vis QE65000 and Ocean Optics NIRQ512 spectrometers were coupled through a bifurcated fiber to the integrating sphere, which provides an effective detection range from 350 to 1700 nm. Each sample solution was degassed and placed in an anaerobic environment prior to the measurement.

The nanosecond transient absorption (TA) spectra and decays, triplet excited-state quantum yields (Φ_{T}), and triplet lifetimes (τ_{TA}) were measured on the laser flash photolysis spectrometer (Edinburgh LP920) in the nitrogen-purged toluene solutions. The third harmonic output (355 nm) of a Quantel Brilliant Nd:YAG laser with 4.1 ns pulse duration and 1 Hz repetition rate was utilized as the excitation source. Each sample solution was purged with nitrogen for 40 min before the measurement. The triplet excited-state molar extinction coefficients (ϵ_{T}) at the TA maxima were deduced using the singlet depletion method.³³ To obtain the triplet quantum yields, the relative actinometry method³⁴ was applied using a silicon naphthalocyanine (SiNc) in benzene solution ($\epsilon_{590\text{ nm}} = 70000\text{ L mol}^{-1}\text{ cm}^{-1}$, $\Phi_{\text{T}} = 0.2$)³⁵ as the reference.

DFT Calculations. All calculations were performed using the Gaussian16 software package.³⁶ The ground-state geometries of the complexes were optimized using density functional theory (DFT).³⁷ The long-range corrected functional CAM-B3LYP³⁸ was used with a mixed basis set of LANL2DZ³⁹ for Ir(III) and 6-31G*⁴⁰ for all other atoms. Solvent effects were incorporated in the calculations by using the conductor like polarizable continuum model (CPCM) reaction field method.⁴¹ Toluene was chosen as the solvent for consistency with the experimental studies.

A linear response time dependent DFT (TDDFT)⁴² methodology was adopted to calculate 70 excited states in toluene using the same functional and basis set as those used for the ground-state calculations. Although our previous joint experimental and computational studies demonstrated that the hybrid functional PBE0⁴³ was capable of accurately representing the excited properties of many Ir(III) complexes,^{12,44} PBE0 failed in reproducing the correct trends for the complexes studied in this work, especially for complexes containing the nitro substituent. It has been discussed in the literature that long-range corrected functionals, such as CAM-B3LYP, more accurately describe the localization/delocalization properties of charge transfer states in the donor–acceptor molecules than hybrid functionals, despite the overall overestimation of the excited energies.^{45,46} As such, we chose CAM-B3LYP for our calculations, while we applied a constant shift of -0.82 eV to correct the blue shift and align the calculated absorption spectra with the experimental spectra. To construct the absorption spectra, each optical transition obtained from TDDFT calculations was broadened by the Gaussian function with a width of $\sigma = 0.08\text{ eV}$, which well reproduces the thermal broadening of the experimental spectra.

Emission energies were calculated by the ΔSCF method.^{47–49} The triplet ground-state geometry was optimized (using the CAM-B3LYP functional and LAN2DS/6-31G* basis set) and then used for TDDFT calculations of the vertical triplet excitations.

To better understand the nature of the excited states, natural transition orbitals (NTOs)⁵⁰ were calculated. NTOs are compact representations of the density of the excited electron–hole pair using diagonalized transition density matrices obtained from the TDDFT

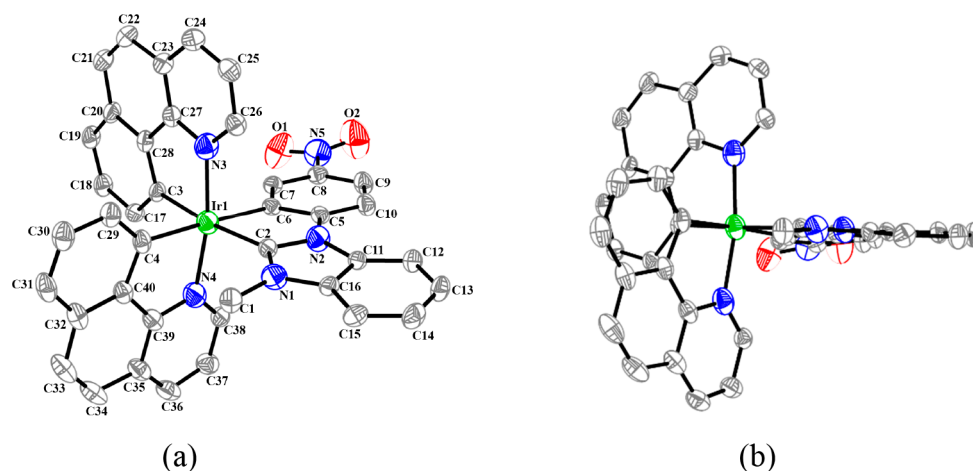


Figure 1. ORTEP (Oak Ridge Thermal Ellipsoid Plot)⁵⁴ diagram displaying thermal ellipsoids at the 50% probability level and atom labels for Ir1. Hydrogen atoms are omitted for clarity. (a) and (b) are viewed from different angles.

calculations. All NTOs were visualized by VMD⁵¹ code using 0.02 isosurface resolution.

X-ray Crystallography. The single crystal of Ir1 was grown by slow diffusion of hexane into a dilute dichloromethane solution of Ir1. The crystallographic data were collected on a Bruker Kappa Apex II Duo X-ray diffractometer with an Apex 2 CCD area detector at 200.01 K. The structure was solved with the ShelXT⁵² structure solution program embedded in Olex2,⁵³ using Intrinsic Phasing, and refined with the ShelXL refinement package with least-squares minimization.

Fabrication and Characterization of the OLEDs. The multilayer OLEDs were fabricated by the vacuum-deposition method. The 95 nm indium tin oxide (ITO) coated glass substrates with a sheet resistance of 15–20 $\Omega \text{ sq}^{-1}$ were subjected to a routine cleaning process of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol in an ultrasonic bath and treated with O_2 plasma for 10 min. Organic layers and the cathode were sequentially deposited on the ITO-coated glass substrates by thermal evaporation under high vacuum ($<5 \times 10^{-4}$ Pa). The deposition rates were 1.0 $\text{\AA s}^{-1}$ for organic layers, 0.1 $\text{\AA s}^{-1}$ for the LiF layer, and 3–5 $\text{\AA s}^{-1}$ for the Al cathode, respectively. The active area of each device was 9 mm^2 . The electroluminescence spectra (EL), the current density–voltage characteristics (J – V), and the current density–voltage–luminance curves (J – V – L) of the OLEDs were detected on a Photo Research SpectraScan PR-745 spectroradiometer and a Keithley 2450 source meter, and the data were recorded simultaneously. All device characterization was carried out at room temperature under ambient laboratory conditions. The device configuration is ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/CBP:10 wt % Ir2 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al, where 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN) is the hole injection layer (HIL), 1-bis[4-[*N,N*-di-4-tolylamino]phenyl]cyclohexane (TAPC) works as the hole-transporting layer (HTL), tris(4-carbazoyl-9-ylphenyl)amine (TCTA) serves as the electron-blocking layer (EBL), 4,4'-bis(9H-carbazol-9-yl)-1,1'-biphenyl (CBP) functions as the host, 1,3,5-tris(*m*-pyrid-3-ylphenyl)benzene (TmPyPB) acts as the electron-transporting layer (ETL) and the hole-blocking layer (HBL), and LiF is the electron injection layer (EIL). The molecular structures of HATCN, TAPC, TCTA, CBP, and TmPyPB are shown in Figure S1 in the Supporting Information.

RESULTS AND DISCUSSION

Single-Crystal Structure of Ir1. A suitable single crystal of Ir1 for X-ray crystallographic analysis was obtained by slow diffusion of hexane into a dilute dichloromethane solution of Ir1 at room temperature. The crystal structure of Ir1 was determined by X-ray diffraction at 200.01 K, and the obtained

Table 1. Selected Bond Lengths ($\text{\AA}$) and Angles (deg) for Ir1

Ir1–N3	2.059(5)	Ir1–C3	2.059(5)
Ir1–N4	2.061(5)	Ir1–C4	2.073(6)
Ir1–C2	2.054(5)	Ir1–C6	2.086(6)
N4–Ir1–C4	80.6(2)	C2–Ir1–C3	171.9(2)
N4–Ir1–C6	97.3(2)	C2–Ir1–C4	101.6(2)
N3–Ir1–N4	169.6(19)	C2–Ir1–C6	77.7(2)
N3–Ir1–C3	80.1(2)	C3–Ir1–N4	92.0(2)
N3–Ir1–C4	92.2(2)	C3–Ir1–C4	86.2(2)
N3–Ir1–C6	89.9(2)	C3–Ir1–C6	94.6(2)
C2–Ir1–N4	91.5(2)	C4–Ir1–C6	177.8(2)
C2–Ir1–N3	97.3(2)		

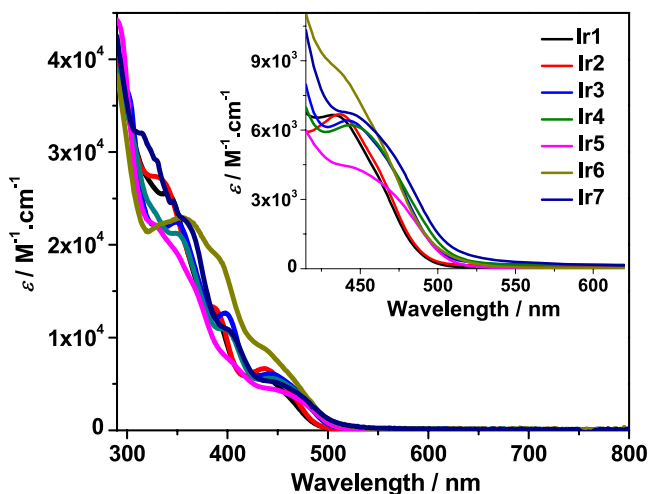


Figure 2. Experimental UV–vis absorption spectra of complexes Ir1–Ir7 at room temperature in toluene. The inset is the expansion of the spectra in the region of 415–620 nm.

crystallographic data are compiled in Table S1 in the Supporting Information.

Figure 1 shows the top-down and side views of the crystal structure for Ir1. The selected bond lengths and bond angles around the Ir(III) center are presented in Table 1. The crystal structure clearly indicates that the N atoms on the C^N ligands coordinate to the metal center in a trans configuration and a

Table 2. Photophysical Properties of Complexes Ir1–Ir7

	$\lambda_{\text{abs}}/\text{nm}$ ($\log \epsilon$) ^a	$\lambda_{\text{em}}/\text{nm}$ ($\tau_{\text{em}}/\text{ns}$); Φ_{em}^b (room temp)	k_r/s^{-1} ^c	$k_{\text{nr}}/\text{s}^{-1}$ ^c	$\lambda_{\text{em}}/\text{nm}^d$ (77 K)	$\lambda_{\text{T1-Tn}}/\text{nm}$ ($\tau_{\text{TA}}/\text{ns}$, $\log \epsilon_{\text{T1-Tn}}$); Φ_{T}^e
Ir1	290 (4.60), 340 (4.41), 386 (4.11), 433 (3.82)	544 (45); 0.0027	2.40×10^5	8.86×10^7	— ^f	532 (50, —); — ^g
Ir2	290 (4.59), 330 (4.44), 387 (4.12), 436 (3.82)	540 (5300); 0.16	1.21×10^5	6.34×10^5	522, 560, 608 (sh.)	502 (5700, —); — ^g
Ir3	290 (4.57), 349 (4.35), 398 (4.11), 442 (3.81)	554 (3520); 0.15	1.85×10^5	1.05×10^6	531, 568, 617 (sh.)	547 (4050, 4.45); 0.23
Ir4	290 (4.59), 349 (4.33), 397 (4.04), 444 (3.79)	549 (2640); 0.064	1.28×10^5	1.87×10^6	519, 551, 597 (sh.)	547 (2430, 4.53); 0.19
Ir5	290 (4.65), 326 (4.35), 391 (3.94), 445 (3.64)	552 (2490); 0.046	1.15×10^5	2.39×10^6	524, 554	550 (2550, 4.57); 0.16
Ir6	290 (4.63), 354 (4.41), 390 (4.27), 433 (3.94)	545 (160); 0.016	3.33×10^5	2.05×10^7	528, 566	523 (160, 4.37); 0.30
Ir7	290 (4.63), 315 (4.51), 355 (4.37), 400 (4.05), 443 (3.72)	552 (4030); 0.088	7.04×10^4	7.30×10^5	534, 569	540 (4000, 4.20); 0.31

^aElectronic absorption band maxima (λ_{abs}) and molar extinction coefficients ($\log \epsilon$) in toluene at room temperature. ^bRoom-temperature emission band maxima (λ_{em}) and lifetimes (τ_{em}) for Ir1–Ir7 in toluene at a concentration of 1×10^{-5} mol L⁻¹. The absolute quantum yields were measured via the Ocean Optics integrating sphere ($\lambda_{\text{ex}} = 450$ nm). The emission signals were integrated in the range of 350–820 nm. ^cRadiative (k_r) and nonradiative decay rates (k_{nr}) in toluene calculated by $k_r = \Phi_{\text{em}}/(\Phi_{\text{T}}\tau_{\text{em}})$ and $k_{\text{nr}} = (1 - \Phi_{\text{em}})/(\Phi_{\text{T}}\tau_{\text{em}})$, respectively. For Ir3–Ir7, the estimated triplet quantum yields (Φ_{T}) from the transient absorption measurement were used. For Ir1 and Ir2, Φ_{T} was assumed to be 0.25. ^dEmission band maxima in MTHF glassy matrix at 77 K. ^eNanosecond TA band maxima ($\lambda_{\text{T1-Tn}}$), triplet excited-state lifetimes (τ_{TA}), molar extinction coefficients ($\epsilon_{\text{T1-Tn}}$), and quantum yields (Φ_{T}) measured in toluene at room temperature. ^fThe emission signal was too weak to be recorded. ^gDue to the lack of a bleaching band, the $\epsilon_{\text{T1-Tn}}$ values were unable to be estimated by the singlet depletion method. Consequently, the Φ_{T} values could not be calculated.

bond angle of 169.6°, which is slightly distorted from the octahedral geometry. The other bond angles around the Ir(III) center also deviate from the angles for an ideal octahedral geometry. In comparison with the Ir(III) complex bearing 1-methyl-3-phenylbenzimidazolylidene and 2-phenylpyridine ligands,²² similar bond angles and bond lengths were found. The Ir–C2 and Ir–C6 bonds in Ir1 were 0.010 and 0.025 Å shorter than the corresponding bonds in the reported complex, while slightly longer Ir–N3 and Ir–N4 bonds of 0.005 and 0.008 Å, respectively, were found in Ir1 in comparison to those in the reported complex. These minor differences are likely due to the rigidity of the cyclometalating benzo[*h*]quinoline ligands. Complexation of the NHC ligand with the metal center prohibited the rotation of the *N*-phenyl substituent, resulting in a nearly coplanar configuration (7.80°) between the phenyl ring and the benzimidazole moiety (Figure S2 in the Supporting Information).

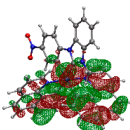
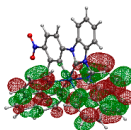
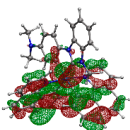
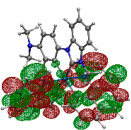
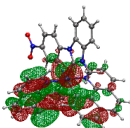
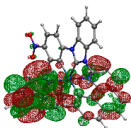
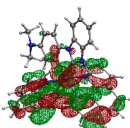
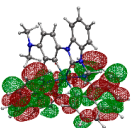
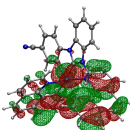
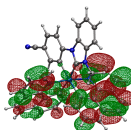
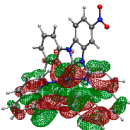
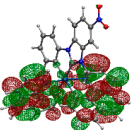
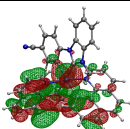
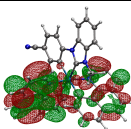
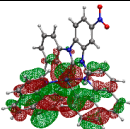
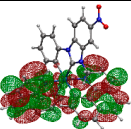
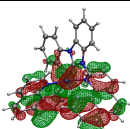
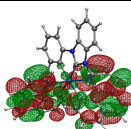
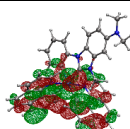
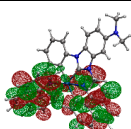
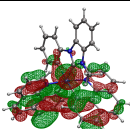
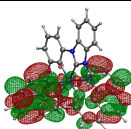
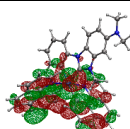
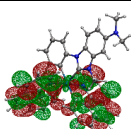
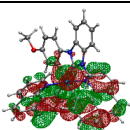
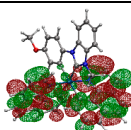
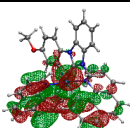
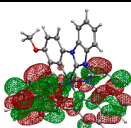
Electronic Absorption. The electronic absorption spectra of complexes Ir1–Ir7 were measured in toluene, dichloromethane, tetrahydrofuran, and acetonitrile. The spectra in toluene are displayed in Figure 2, and the absorption band maxima and molar extinction coefficients are compiled in Table 2. The normalized absorption spectra in the other solvents are presented in Figure S3 in the Supporting Information. The concentration-dependence study from 5×10^{-6} to 1×10^{-4} mol L⁻¹ showed that the absorption of these complexes in toluene obeyed Beer's law without forming ground-state aggregates. All complexes possessed intense absorption bands ($\epsilon \approx 10^4$ L mol⁻¹ cm⁻¹) in the wavelength range of 290–420 nm and a broader and weaker band ($\epsilon \approx 10^3$ L mol⁻¹ cm⁻¹) at 420–500 nm. Taking into account the spectral features and the molar extinction coefficients, we tentatively assign the 290–420 nm bands predominantly to spin-allowed ligand-localized ¹ π,π^* transitions. For the 420–500 nm band, the structureless feature suggests charge transfer transitions. However, the moderate molar extinction coefficient implies significant contributions of the ¹ π,π^* transitions. Attribution of the major absorption bands, including the absorption band centered at 433–445 nm, to predominant ¹ π,π^* transitions is supported by the minor solvatochromic

effect of these complexes in solvents with varied polarities, which is a characteristic of ¹ π,π^* transitions (see Figure S3 in the Supporting Information). These assignments are also confirmed by the TDDFT calculations that will be discussed in the following paragraph. In addition, all complexes exhibited very weak absorption tails beyond 500 nm. With reference to the other reported Ir(III) complexes with NHC ligands,²² we attribute this tail to spin-forbidden charge transfer transitions (³MLCT/³LLCT).

To better understand the natures of the electronic transitions, TDDFT calculations were carried out for complexes Ir1–Ir7 in toluene. The spectral features and the trend of the calculated spectra matched the experimental spectra very well (Figures S4 and S5 in the Supporting Information). The natural transition orbitals (NTOs) for the electrons and holes corresponding to the lowest-energy electronic transitions are provided in Table 3, and the NTOs corresponding to the transitions contributing to the high-energy major absorption bands are provided in Tables S2 and S3 in the Supporting Information. As the NTOs in Table 3 show, the predominant contributors to the low-energy absorption band at ca. 440 nm are the C[^]N ligand-localized ¹ π,π^* transition, admixing with a ¹MLCT (metal-to-ligand charge transfer) transition. In addition, ¹LLCT (ligand-to-ligand charge transfer), ¹LMCT (ligand-to-metal charge transfer), and ¹d,d transitions also made minor contributions. The NTOs indicate that the NHC ligand essentially is not involved in the low-energy transitions. Therefore, introducing electron-donating or -withdrawing substituents to the NHC ligand has a minor effect on the low-energy absorption band at ca. 440 nm. Nevertheless, electron-donating substituents, such as OCH₃ and N(CH₃)₂ groups, induced a slight red shift of the low-energy absorption band in Ir4, Ir5, and Ir7 regardless of whether the substituent was introduced at the phenyl ring or at the benzimidazole motif. In contrast, electron-withdrawing substituents, such as CN and NO₂ groups, caused a slight blue shift of the low-energy absorption band in Ir1, Ir2, and Ir6.

The NTOs in Table S2 in the Supporting Information show that the transitions in the region of 380–425 nm have predominant ¹ π,π^* /¹LLCT/¹MLCT characters, with the

Table 3. NTOs of the Holes and Electrons for the Low-Energy Transitions in Ir1–Ir7, Calculated by the TDDFT Method with the CAM-B3LYP Functional and LANL2DZ/6-31G* Basis Set in Toluene

Excited states and properties	Hole	Electron	Excited states and properties	Hole	Electron
Ir1 S ₁ 444 nm <i>f</i> = 0.155			Ir5 S ₁ 451 nm <i>f</i> = 0.136		
					
Ir2 S ₁ 444 nm <i>f</i> = 0.154			Ir6 S ₁ 445 nm <i>f</i> = 0.153		
					
Ir3 S ₁ 449 nm <i>f</i> = 0.144			Ir7 S ₁ 452 nm <i>f</i> = 0.139		
					
Ir4 S ₁ 449 nm <i>f</i> = 0.144					
					

contribution from the ¹LLCT ($\pi(\text{NHC}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N})$) transition becoming more significant. Similar to the case for the lowest-energy absorption band at ca. 440 nm, electron-donating substituents caused a red shift of the 380–425 nm band while electron-withdrawing substituents induced a blue shift. For the high-energy absorption bands at <380 nm, they are also composed of mixed ¹ $\pi, \pi^*/^1\text{CT}/^1\text{d}, \text{d}$ transitions, with the holes or electrons becoming more delocalized and thus the oscillator strengths being increased.

Photoluminescence. The emission of complexes Ir1–Ir7 was studied in different solvents at room temperature. The emission spectra in deaerated toluene are displayed in Figure 3, and the emission parameters, i.e. the emission quantum yields (τ_{em}) and lifetimes (Φ_{em}), are given in Table 2. All complexes exhibited long-lived (several microseconds except for Ir1 and Ir6) and oxygen-sensitive bright yellow luminescence with large red shifts in comparison to their corresponding excitation wavelength, suggesting the phosphorescent nature of the

emission. The normalized emission spectra and the emission characteristics in other solvents are provided in Figure S6 and Table S4 in the Supporting Information, respectively. Comparison of the experimental and calculated emission energies of Ir1–Ir7 in toluene is provided in Figure S7 in the Supporting Information. The emission spectra for all complexes are broad and featureless, indicative of charge-transfer characters. On the other hand, the emission energies in all solvents are quite similar, which is a characteristic of ³ π, π^* emission. Moreover, the emission energies of all complexes resemble each other, suggesting the similar nature of the emitting states. However, the longer lifetimes of Ir2 in comparison to those of the other complexes in each corresponding solvent along with the clearer vibronic structure in toluene imply a somewhat larger contribution of the ³ π, π^* character in the emitting state of Ir2.

The NTOs in Table 4 indicate that the holes of the T₁ states in all complexes are delocalized on one of the C[^]N ligands and

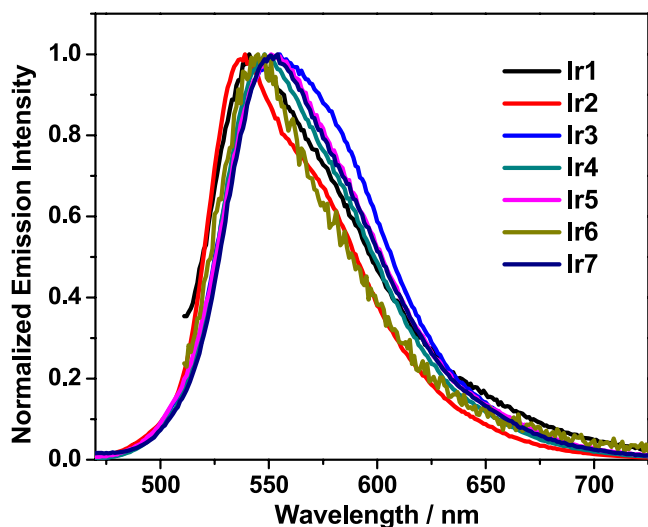


Figure 3. Experimental emission spectra of complexes **Ir1** ($\lambda_{\text{ex}} = 434$ nm), **Ir2** ($\lambda_{\text{ex}} = 437$ nm), **Ir3** ($\lambda_{\text{ex}} = 442$ nm), **Ir4** ($\lambda_{\text{ex}} = 444$ nm), **Ir5** ($\lambda_{\text{ex}} = 445$ nm), **Ir6** ($\lambda_{\text{ex}} = 433$ nm), and **Ir7** ($\lambda_{\text{ex}} = 444$ nm) in deoxygenated toluene at room temperature.

Table 4. NTOs Contributing to the T_1 States of Complexes **Ir1–Ir7** in Toluene, Calculated by the $\Delta\text{SCF-TDDFT}$ Method Using the CAM-B3LYP Functional and LANL2DZ/6-31G* Basis Set

T_1 Energy (nm) ^a	Hole	Electron	T_1 Energy (nm) ^a	Hole	Electron
Ir1 545			Ir5 548		
Ir2 545			Ir6 545		
Ir3 546			Ir7 548		
Ir4 547					

^aThe emission energies were calculated by ΔSCF method.

the d orbital of the Ir(III) ions, while the electrons are mainly distributed on the same C[^]N ligand. Therefore, the emission of these complexes predominantly emanates from the $^3\pi, \pi^*/^3\text{MLCT}$ ($d(\text{Ir}) \rightarrow \pi^*(\text{C}^{\wedge}\text{N})$) states.

To further confirm the nature of the emitting states in **Ir1–Ir7**, emission of these complexes in a glassy matrix of 2-methyltetrahydrofuran (MTHF) at 77 K was studied and the emission band maxima are given in Table 2. A comparison of the emission spectrum of each complex (except for **Ir1**, in which the emission at 77 K was too weak to be monitored) in fluid MTHF solution at room temperature and in an MTHF glassy matrix at 77 K is provided in Figure S8 in the Supporting Information. The emission spectra of these complexes at 77 K were all blue-shifted and became structured. The vibronic progressions were in the range of 1033–1410 cm^{-1} , which are in line with the ring stretching modes of the aromatic rings. In addition, the thermally induced Stokes shifts for these complexes were in the range of 489–836 cm^{-1} . These features are consistent with the predominant $^3\pi, \pi^*/^3\text{MLCT}$ nature of the emitting states in these complexes.

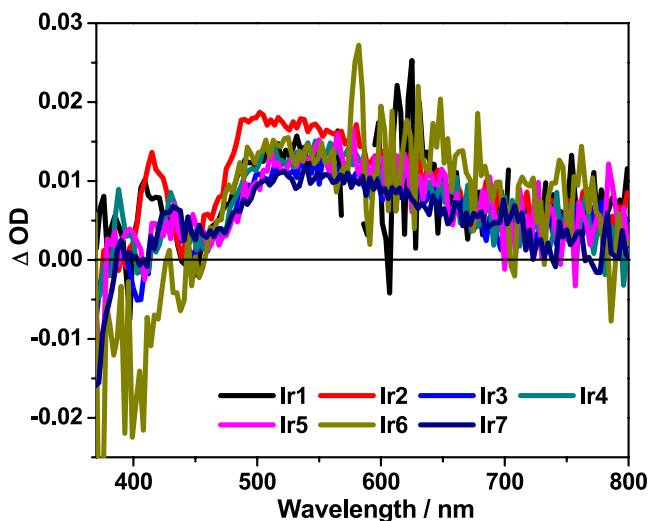


Figure 4. Nanosecond transient absorption spectra of complexes **Ir1–Ir7** in deaerated toluene immediately after 355 nm excitation ($A_{355\text{ nm}} = 0.4$ in a 1 cm cuvette).

Table 5. Summary of the Ir2-Based OLED Performance

V_{on} (V) ^a	L (cd/m^2) ^b	η_{C} (cd/A) ^b	η_{P} (lm/W) ^b	EQE (%) ^b
2.9	32747	71.29	68.90	20.6

^a V_{on} is the turn-on voltage at 1 cd/m^2 . ^bThe luminance (L), current efficiency (η_{C}), power efficiency (η_{P}), and EQE are the maximum values of the device.

Although the emission energies and natures for these complexes are similar and the NHC ligand is not involved in the emitting state, the substituents on the NHC ligand still exerted minor effects on the emission energies. Electron-withdrawing substituents caused a slight blue shift of the emission bands in **Ir1**, **Ir2**, and **Ir6** in comparison to that in **Ir3**, while electron-donating substituents had a negligible effect on the emission energies of **Ir4**, **Ir5**, and **Ir7**. In contrast, the effects of the substituents at the NHC ligand on the emission lifetimes and quantum yields are drastic. An examination of the emission parameters given in Table 2 and Table S4 in the Supporting Information found that complexes **Ir1** and **Ir6**, which contain the strongly electron-withdrawing nitro substituent, exhibited much shorter emission lifetimes and much weaker emission in comparison to those of the other complexes regardless of the solvent used. While the electron-donating substituents OCH_3 and $\text{N}(\text{CH}_3)_2$ also reduced the emission lifetimes and quantum yields in **Ir4**, **Ir5**, and **Ir7** with respect to those in **Ir3**, the reductions were generally more pronounced in **Ir5** and **Ir7**, which contain the more strongly electron-donating substituent $\text{N}(\text{CH}_3)_2$. Interestingly, the longest emission lifetime and strongest emission were found in **Ir2**, which bears an electron-withdrawing CN substituent.

The effects of the substituents on the emission lifetimes and quantum yields can be rationalized by the different influences of the substituent on the radiative decay rate constant (k_{r}) and nonradiative decay rate constants (k_{nr}) for these complexes. The k_{r} and k_{nr} data given in Table 2 indicate that the different substituents at the NHC ligand do not change the k_{r} values significantly (~ 4.7 -fold), while they alter the k_{nr} values by approximately 140-fold. The CN-substituted complex **Ir2** possesses the lowest k_{nr} value but a comparable k_{r} value with

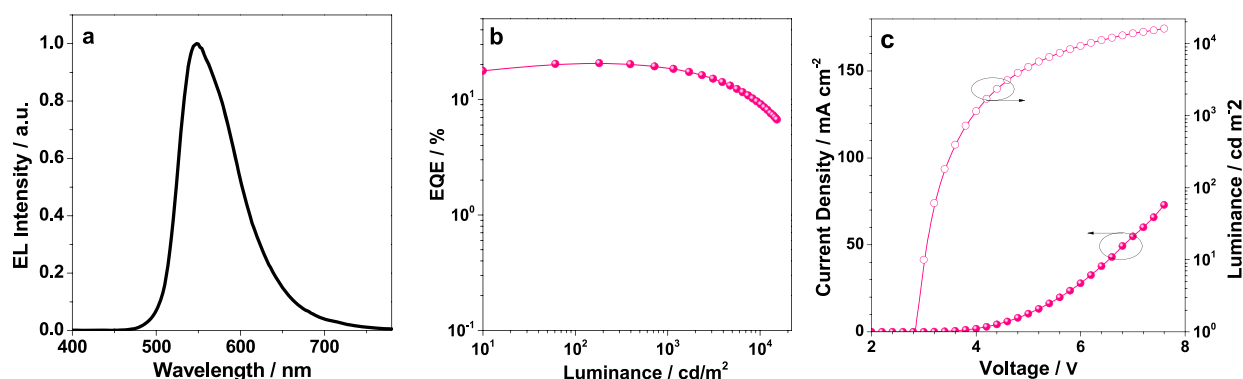


Figure 5. Electroluminescence device data: (a) EL spectrum; (b) EQE– L curve; (c) J – V – L curves. Device architecture: ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/CBP:10 wt % Ir2 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al.

respect to the other complexes, resulting in the strongest emission and longest lifetime among this series of complexes.

It is also worth noting that although the π -extended rigid benzo[*h*]quinoline C^N ligand lowered the emission energies of Ir1–Ir7, it prolonged the emission lifetimes for most of the complexes in all solvents (except for Ir1 and Ir6 in toluene, see Table S4 in the Supporting Information) by approximately 1 order of magnitude in comparison to that of the most relevant Ir(III) complex (0.69 μ s in MTHF) reported in the literature, which bears the 3-methyl-1-phenylbenzimidazol-3-ium NHC ligand and more flexible 2-phenylpyridine C^N ligands.²⁷ The prolonged lifetimes should be attributed to the drastically reduced k_{nr} values and/or k_r values in Ir1–Ir7. For example, the k_{nr} and k_r values for Ir3 (which has the same NHC ligand as that in complex 6 in ref 27) in THF are 4.17×10^5 and 1.18×10^5 s^{−1}, respectively, while these values for complex 6 in ref 27 in MTHF are 5.10×10^6 and 1.20×10^6 s^{−1}, respectively, assuming the same triplet quantum yield of 0.23 as that for Ir3. Apparently, replacing the more flexible 2-phenylpyridine ligand by the rigid benzo[*h*]quinoline ligand dramatically reduced the k_{nr} and k_r values for Ir3 in comparison to those of complex 6 in ref 27, resulting in a much longer lifetime (8.14 μ s for Ir3 in THF vs 0.69 μ s for complex 6 in ref 27 in MTHF) and slightly increased the emission quantum yield for Ir3 (0.22 in THF vs 0.19 for complex 6 in ref 27 in MTHF). An increased emission quantum yield and/or emission lifetime due to the incorporation of a rigid C^N or N^N ligand in Ir(III) complexes has been previously reported by our group for the monocationic Ir(N^N)(C^N)₂⁺-type complexes.^{55–57} Similar results are observed for the neutral Ir(NHC)(C^N)₂ type complexes reported in this work.

Transient Absorption (TA). To further explore the triplet excited-state characteristics of complexes Ir1–Ir7, a TA study was carried out in deaerated toluene solutions for all complexes. The TA spectra of Ir1–Ir7 immediately after 355 nm excitation are shown in Figure 4, and the time-resolved spectra are provided in Figure S9 in the Supporting Information. The TA band maxima, the triplet excited state lifetimes, and quantum yields are summarized in Table 2. The TA spectral features of all complexes resemble each other, all exhibiting a broad structureless positive absorption band in the region of 460–700 nm. However, the TA band maxima differ slightly, with electron-withdrawing substituents, especially the CN substituent, causing a noticeable blue shift, while electron-donating substituents showing a minor effect in comparison to that of Ir3. The major difference appeared at 380–450 nm, probably due to the different ground-state absorption in this

region. The triplet lifetimes deduced from the decay of TA signals matched well with the respective lifetimes obtained from the decay of emission signals, implying that the transient absorbing excited states are the emitting excited states: i.e., the C^N ligand-centered ³ π, π^* state mixed with ³MLCT configurations.

Phosphorescent OLEDs (PhOLEDs). Among this series of complexes, Ir2 possessed the highest emission quantum yields in all of the solvents studied. Thus, we chose this complex as the emitter for fabrication of a prototype electroluminescence (EL) device. The device architecture consisted of ITO/HATCN (5 nm)/TAPC (25 nm)/TCTA (5 nm)/CBP:10 wt % Ir2 (20 nm)/TmPyPB (55 nm)/LiF (1 nm)/Al. The data for the device performances, such as the luminance (L), current efficiency (η_c), power efficiency (η_p), and EQE, are summarized in Table 5. The obtained EL spectrum, EQE– L curve, and J – V – L curves are shown in Figure 5. The EL spectral feature and the emission band maximum (548 nm) resemble those of its photoluminescence in CH₂Cl₂, THF, and CH₃CN solutions (Figure S6 in the Supporting Information). Thus, the parentage of the EL is assigned to the triplet excited state of the dopant: namely, the ³MLCT/³ π, π^* state. The turn-on voltage (V_{on}) of this device was 2.9 V. In terms of the brightness, the maximum current efficiency (η_c) and external quantum efficiency (EQE) are 71.29 cd A^{−1} and 20.6%, respectively. Note that the device did not suffer from serious efficiency roll-off even at high brightness (Figure 5b). In comparison to the performance of a blue OLED using (2-(2,4-difluorophenyl)pyridine)₂Ir(NHC) as the emitter,²² the OLED based on Ir2 exhibited a lower turn-on voltage, doubled η_c and EQE, and almost 4-fold higher maximum luminance. These results demonstrate the potential of using these types of complexes as yellow emitters for OLED applications.

CONCLUSIONS

Seven neutral cyclometalated Ir(III) complexes bearing the benzo[*h*]quinoline C^N ligand and different 1-phenylbenzimidazole (NHC) ancillary ligands with substituents at the C4' of the phenyl ring or C5 of the NHC ligand were synthesized and characterized. The influence of the electron-donating or -withdrawing substituents on their photophysical properties was investigated. All complexes exhibit ¹ $\pi, \pi^*/^1$ CT/¹d,d transitions at ca. 440 nm and yellow ³ $\pi, \pi^*/^3$ MLCT emission at room temperature in fluid solutions. They all exhibited broad triplet transient absorption at 460–700 nm with similar

spectral features. Generally, electron-withdrawing substituents caused minor blue shifts of the low-energy absorption band and the emission band, while the electron-donating substituents induced red shifts somewhat. Although the effects of the substituents at the NHC ligand on the T_1 state energies of these complexes are quite minor, the effects on the T_1 lifetimes and emission quantum yields are drastic. The most emissive complex, **Ir2**, was utilized as the dopant for PhOLED fabrication. The obtained device displayed a yellow emission with a maximum current efficiency of 71.29 cd A^{-1} , a maximum luminance of 32747 cd m^{-2} , a maximum EQE of 20.6%, a low turn-on voltage (2.9 V), and a low efficiency roll-off. In comparison to the reported blue OLED using (2-(2,4-difluorophenyl)pyridine)₂Ir(NHC) as the emitter, the OLED based on **Ir2** exhibited a lower turn-on voltage, doubled η_c and EQE, and almost 4-fold higher maximum luminance. These results demonstrate the potential of using these types of complexes as yellow emitters for OLED applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b01678.

Molecular structures of HATCN, TAPC, TCTA, CBP, and TmPyPB, crystallographic data of single crystal of **Ir1**, schematic view of the dihedral angle between the phenyl ring and the benzimidazole moiety in the crystal structure of **Ir1**, comparison of the experimental and calculated UV–vis absorption spectra of complexes **Ir1**–**Ir7** in toluene, normalized UV–vis absorption and emission spectra of **Ir1**–**Ir7** in different solvents, comparison of the emission spectra of **Ir1**–**Ir7** and the calculated emission energies, the natural transition orbitals (NTOs) representing transitions contributing to the major absorption bands of **Ir1**–**Ir7**, the emission characteristics of **Ir1**–**Ir7** in different solvents, comparison of the emission spectra of **Ir2**–**Ir7** in MTHF at room temperature and 77 K, the time-resolved nanosecond transient absorption spectra of **Ir1**–**Ir7** in toluene, and the full author list for ref 36 (PDF)

Accession Codes

CCDC 1923140 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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