New, Reliable Thienothiophenyl-isoquinoline Iridium complex-based Deep Red to Near-Infrared Organic Light-Emitting Diodes with Low Driving Voltage and High Radiant Emittance for Practical Biomedical Applications

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Keywords

new thienothiophenyl-isoquinoline iridium complex, near-infrared, radiant emittance, low driving voltage, cell proliferation effect
Abstract

It is extremely rare that near-infrared organic light-emitting diodes (NIR OLEDs) have been actually applied to various fields like sensors, night-vision displays, or phototherapy owing to device reliability and stability. Hence, developing a novel deep red to NIR (DR/NIR) emitter for the high-performance DR/NIR OLED has become a prominent research area. Herein, a novel thienothiophene-isoquinoline-based Ir(III) complex DR/NIR emitter with narrow full-width half maximum (FWHM, 38 nm), a shallow highest occupied molecular orbital (HOMO) energy level and short radiative lifetime of 0.66 μs was designed and synthesized. Our best device based on a new Ir(III) complex yielded record high radiant emittance (> 5 mW cm⁻²) at low voltage (6 V), low external quantum efficiency (EQE) roll off, low driving-voltage (2.5-6 V), and stable operational lifetime for biomedical application with an emission peak wavelength of 696 nm. From all perspectives, this was notably outstanding performance among other reported Ir(III)-based DR/NIR OLEDs. Moreover, DR/NIR OLEDs were applied to the biomedical field and an in-vitro experiment showed an increase in cell proliferation effect of up to 24% under diverse conditions.
Introduction

Organic light-emitting diodes (OLEDs) have become mainstream as the next generation of wearable displays that will outperform lasers and light-emitting diodes (LEDs). Recently, OLED-based platforms used for light applications were introduced.\cite{1-3} In particular, DR/NIR OLEDs have emerged in the past few years because they can be applied for night vision displays, optical sensors, and phototherapy.\cite{4} However, DR/NIR emitters exhibit intrinsic defects: these emitters are prone to undesired non-radiative decay pathways owing to the narrow bandgap. According to the energy-gap law, the nonradiative decay rate ($k_{nr}$) is inversely proportional to the band gap. Besides this, the radiative rate ($k_r$) has a cubic dependence on the transition energy, so that it is expected to get smaller for lower-energy emitters, implying that DR/NIR emitters have poor quantum efficiencies because of the incorporation of ground- and excited-vibrational energy states.\cite{5-9} Consequently, research on high efficiency DR/NIR OLEDs has lagged behind that on visible-region OLEDs. To overcome this limitation, diverse ways of boosting the DR/NIR efficiency were introduced. In general, there are three kinds of DR/NIR emitters for high efficiency DR/NIR OLEDs: donor-acceptor-donor (D-A-D) type,\cite{10,11} thermally activated delayed fluorescence (TADF),\cite{12-15} and transition-metal complexes.\cite{16,17} DR/NIR fluorophores of the D-A-D type have been researched to provide DR/NIR OLEDs with cost advantage and versatility. However, most DR/NIR OLEDs based on the D-A-D type show extremely low EQE, radiance, and unexplained operational lifetime for practical application.\cite{10,11} TADF DR/NIR emitters utilize nonradiative triplet excitons that move to a singlet region and achieve 100% internal quantum efficiency (IQE).\cite{18} Nonetheless, there are chronic constraints with fluorescence quenching. Hence, TADF-based DR/NIR OLEDs have a low luminance value. Meanwhile, high-efficiency DR/NIR OLEDs using transition metal complexes such as osmium (Os),\cite{19-21} platinum (Pt),\cite{22-26} and iridium (Ir)\cite{27-38} have been introduced recently. They exhibit better performance with regard to EQE and radiant emittance than prior methods. Among the research published on DR/NIR OLEDs, a Pt-complex-based NIR OLED was reported with the highest record of EQE and radiant emittance.\cite{22} Despite this world-record,
there is still the need to overcome reliability issues, such as driving voltage and lifetime, to achieve practical application. Even if the radiant emittance is high, problems with power consumption could occur in the actual application stage if the driving voltage is too high. Actually, there have been no cases of applying a DR/NIR OLED to the biomedical field due to these problems. In general, bio-applications use wavelengths in the 600-700 nm region or long wavelength regions above 780 nm. Moreover, biomedical application is important to view it from the perspective of radiant emittance, not from that of device efficiency. Based on previous works that reported good synergetic effects at specific wavelengths, we designed the novel DR/NIR emitter.

In Figure 1, we report a novel Ir(III) complex designed using thieno[3,2-b]thiophen-isoquinoline-based chelating ligands. The thienothiophene moiety, containing a fused thiophene structure, has a more rigid structure and extended conjugation length, which could be suitably employed to lower the band gap required for DR/NIR emitters. In addition, the high electron density of thienothiophene strengthens the covalent bond between the chelating ligand and iridium, which could improve the operational lifetime and lower the driving voltage. Also, by employing an isoquinoline group instead of a pyridine ring, we can expect an additional red shift of over 100 nm. Furthermore, a heteroleptic iridium complex using 2,2,6,6-tetramethyl-3,5-heptanedione as an ancillary ligand was developed to increase the quantum efficiency for high horizontal orientation. Hence, we can effectively design a DR/NIR OLED that has low driving voltage and high radiant emittance for practical biomedical applications.

Results and discussion

Synthesis and Characterization

The iridium complex was synthesized using the synthetic route shown in Scheme 1. The cyclometalating ligand, 1-(thieno[3,2-b]thiophen-2-yl)isoquinoline (2) was synthesized via typical Suzuki coupling reactions between thieno[3,2-b]thiophen-2-ylboronic acid and 1-
chloroisoquinoline. A $\mu$-chloro-bridged dimer was synthesized through the well-known Nonoyama reaction and base-mediated ligand exchange from iridium chloride hydrates ($\text{IrCl}_3 \cdot \text{nH}_2\text{O}$) and 1-(thieno[3,2-b]thiophen-2-yl)isoquinoline (2). Then, (ttiq)$_2\text{Ir(tmd)}$ was prepared from Ir(III) dimer [(ttiq)$_2\text{Ir(\mu-Cl)}$]$_2$ and 2,2,6,6-tetramethyl-3,5-heptanedione. This pure iridium complex was characterized via $^1\text{H}$NMR, $^{13}\text{C}$NMR spectroscopy, and high-resolution mass spectroscopy. All intermediate compounds were also confirmed by identical methods (see Support Information Figures S1-10). The thermal stability of the new (ttiq)$_2\text{Ir(tmd)}$ complex was studied using TGA thermogram and DSC. The new (ttiq)$_2\text{Ir(tmd)}$ complex showed thermal stability up to 325 °C and did not show any transition up to 250 °C. This supports the notion that the complex shows sufficient thermal stability for use in OLEDs. The electrochemical property of (ttiq)$_2\text{Ir(tmd)}$ was measured using cyclic voltammetry with 0.1 M tetrabutylammonium perchlorate in dichloromethane solution. The HOMO level was calculated to be -4.95 eV, and the shallow HOMO energy level may have resulted from the electron-rich thienothiophene unit.

Photophysical Properties

The UV-visible absorption and photoluminescence spectra of Ir(ttiq)$_2\text{tmd}$ in solution and as vacuum-deposited thin-film are both shown in Figure 2. The intense absorption band below 450 nm can be assigned to the spin-allowed $\pi-\pi^*$ transitions. The relatively weak absorption band in the range of 500-620 nm in both conditions corresponds to mixed $^1\text{MLCT}$ and $^3\text{MLCT}$ (singlet and triplet metal-to-ligand charge transfer) with an $^1\text{ILCT}$ (inter-ligand charge transfer). It is notable that the MLCT bands of Ir(ttiq)$_2\text{tmd}$ represent red-shifted absorption. The band gap was calculated and found to be about 2.13 eV at the band edge. The photoluminescence (PL) spectra of Ir(ttiq)$_2\text{tmd}$ in THF at 77 K shows an emission peak of 704 nm. Meanwhile, the emission peaks in CH$_2$Cl$_2$ solution and in vacuum-deposited thin-film at room temperature (298 K) were observed at 690 nm with a shoulder at 742 and at 696 nm with a shoulder at 750 nm. The emission peak of Ir(ttiq)$_2\text{tmd}$ was red-shifted by about 60 nm compared to that of the well-known red-emitter Ir(piq)$_2$(2,2,6,6-
tetramethylheptane-3,5-dione,

which may due to increased electron density as well as effective extension of the conjugative structure of the cyclometalating ligand, 1-(thieno[3,2-b]thiophen-2-yl)isoquinoline. The absolute photoluminescence quantum yields (PLQY) of solution and thin-film were 15% and 24%, respectively. The PL decay curve of Ir(ttiq)_2tmd in DCM solution is shown in Figure S11; radiative lifetime (\(\tau_{rad}\)) is 0.66 \(\mu\)s. The radiative (\(k_r\)) and nonradiative (\(k_{nr}\)) transition rates are obtained from PLQY and radiative lifetime (\(\tau_{rad}\)). All quantities are summarized in Table 1.

Electroluminescence (EL) Performance

Based on the photoluminescence of the novel Ir(III) complex, devices were fabricated in the following configuration: indium tin oxide (ITO) / molybdenum(VI) oxide (MoO_3, 10 nm) / N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB, 40 nm) / Host: Ir(ttiq)_2tmd (30 nm, 10wt%) / bathophenanthroline (Bphen, 20 nm) / Liq (1 nm) / Al (100 nm); Device 1 (Host: mCP); Device 2 (Host: Bebq_2). Device 3 without an ETL, with a bilayer structure, was fabricated in the following configuration: ITO / MoO_3 (10 nm) / NPB (40 nm) / Bebq_2: Ir(ttiq)_2tmd (50 nm, 10wt%) / Liq (1 nm) / Al (100 nm), where MoO_3, NPB, Bphen, and Liq were the hole injection layer (HIL), hole transport layer (HTL), electron transport layer (ETL), electron injection layer (EIL), respectively, and Al was used as a cathode. All devices were encapsulated within multiple, thin, inorganic layers composed of Al_2O_3 and TiO_2 (30 nm) using the atomic layer deposition (ALD) process.

The energy level alignments and structural configuration of each device are shown in Figures S12–14 (Supporting Information), respectively. The doping concentration and thickness of each layer were optimized for charge balance and exciton confinement. All devices have the same EL spectra at 696 nm as the PL spectra, as shown in Figure 3d. Therefore, excitons were not generated at adjacent layers and condensed well within the emissive layer. The angular dependency and spectra at 10 mA cm\(^{-2}\) of all devices are shown in Figures S15-17 (Supporting Information), respectively.

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All devices have the same light distribution (i.e., Lambertian) and we could easily calculate the total radiant emittance of each device.

The mCP and Bebq₂ have been widely used for host material to transfer energy from host to dopant.⁴⁷ However, Device 1 performed poorly owing to triplet-triplet annihilation between host and dopant and exciton quenching on the grounds of high triplet energy in the mCP compared to the Bebq₂ (T₁ of mCP : 2.9 eV, Bebq₂ : 2.5 eV). Therefore, Devices 2 and 3 gave outperformed Device 1. Device 2 showed the best electrical properties by comparison with the bilayer structure of Device 3 because bphen has a deep HOMO level (Figure S13, Supporting Information). Thus, bphen has a significant role of blocking holes from the emission layer to the cathode, which causes exceptional confinement of excitons in the emissive layer. The current density-voltage, radiant emittance-voltage, and EQE-luminance curves of all devices are shown in Figures 3a-c. The driving voltage of all devices is much lower than for other reported DR/NIR OLEDs.¹⁰,²²,²⁷,³¹ The result may be explained by the shallow HOMO energy level of the new iridium complex. In addition, Device 2 showed the best performance of high radiant emittance of about 6 mW cm⁻² at 6 V and a maximum EQE of 2.75%. Radiant emittance was an underestimated value because EL spectra at > 780 nm was not measured due to equipment limitations. Moreover, the device structure affected the operational lifetime at each radiant emittance. The lifetime during which relative luminance falls from 100 to 50% called the Lethal Time 50, or LT 50, of Device 1 was about 20 h at 0.5 mW cm⁻², as shown in Figure 4a. However, when considering charge transfer and exciton confinement, Devices 2 and 3 achieved better performance owing to optimal structures, as shown in Figures 4b,c. Among all the devices, the best one had a long LT 50 of 4 h at 5 mW cm⁻², 90 h at 3 mW cm⁻², and several hundred hours at low radiant emittance, as shown in Figure 4b.

Figure 5 summarizes the EQE, radiant emittance, and V on of representative Ir(III)-based DR/NIR OLEDs. The EQE value of an optimized device is not very high compared to other DR/NIR OLEDs, as shown in Figure 5a. However, from the perspective point of radiant emittance (Figure 5b) and device reliability such as V on (Figure 5c) and operational lifetime (Figure 4b) for
biomedical application, we obtained the competitive DR/NIR OLED. Figure 5d shows the DR/NIR OLED operating at high radiant emittance.

2.4. Cell-based In-vitro Experiment

Our group has been using OLED to irradiate cells and conducting research on its effects in various ways.\textsuperscript{[2,39,48]} Likewise, we verified the cell proliferation effect using our Ir(III)-based DR/NIR OLED in diverse conditions. Normal human fibroblasts were sprinkled on 96-well plates. An OLED jig designed by our group was used for the cell experiment in order to irradiate the cells with light. It was designed to provide irradiation 1.5 cm from the fibroblast cells and was used to irradiate in a 96-well plate under three conditions including the control. Through this in-vitro experiment, irradiation at the radiant emittance of 1.5 or 3 mW cm\textsuperscript{-2} was applied for 10, 20, and 30 min, respectively, and with the control, to verify cell cytotoxicity. According to ISO 10993-5 standards, cell viability exceeded 70\% and passed the standard under all experimental conditions, as shown in Figure 6a. After that, DR/NIR OLEDs were irradiated in the same manner as in the existing cytotoxicity test to confirm cell proliferation. As a result, as the exposure time increases, the cell proliferation effect rises in each condition. In particular, a cell proliferation effect of 24\% compared to the control group was observed with irradiation for 30 min at 1.5 mW cm\textsuperscript{-2}, as shown in Figure 6b.

**Conclusion**

In summary, novel Ir(III)-based DR/NIR OLED were designed and synthesized to produce a DR/NIR emission and low driving voltage for biomedical application. The newly-developed thieno[3,2-b]thiophen-isoquinoline-based chelating ligand, which enhanced the electron density and extended the conjugation length, is expected to narrow the energy gap in the longer wavelength region of DR/NIR emission. The maximum EQE of the our newly-fabricated DR/NIR OLED was 2.75\%, which is the best performing among the reported DR/NIR OLEDs based on the Ir(III)
complex. Moreover, the new Ir(III)-based DR/NIR OLED has proven reliable by optimizing the structure to ensure sufficient lifetime at actual bio-applicable radiant emittance. We confirmed a cell proliferation effect of up to 24% after irradiating our new Ir(III)-based DR/NIR OLED. It can accurately irradiate the target wavelength even when applied to actual human skin because our device has no angle dependence. Moreover, there are ample possibilities and room for its practical application in biomedical fields.
Methods

General information and Materials: All starting materials were purchased from Aldrich and Alfa Aesar. Tetrakis(triphenylphosphine)palladium(0) was purchased from Boom King. All reagents purchased commercially were used without further purification. Tetrahydrofuran (THF) was dried over sodium and benzophenone, and thieno[3,2-b]thiophen-2-ylboronic acid (1) was prepared according to the literature.[49]

Measurement: The $^1$H NMR and $^{13}$C NMR spectra were recorded using a Bruker 300 MHz and a DRX 500 MHz spectrometer. Mass spectra were measured using a Jeol JMS-700. The thermal analysis measurements were performed using a TA 2050 TGA for thermogravimetric analysis under nitrogen gas. The samples were heated at 10 °C min$^{-1}$. Differential scanning calorimetry was conducted under nitrogen using a TA Instruments 2100 DSC. The sample was heated at 10 °C min$^{-1}$ from 0 to 350 °C. UV-vis absorption spectra were measured using a PerkinElmer LAMBDA-900 UV/vis/IR spectrophotometer. Cyclic voltammograms of materials were recorded on an Epsilon E3 at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu$_4$NClO$_4$) in acetonitrile under nitrogen gas at a scan rate of 50 mV s$^{-1}$. A Pt wire was used as the counter electrode and an Ag/AgCl electrode as the reference electrode.

Synthesis of 1-(thieno[3,2-b]thiophen-2-yl)isoquinoline (2): Thieno[3,2-b]thiophen-2-ylboronic acid (7.27 g, 39.73 mmol), 1-chloroisooquinoline (5 g, 30.56 mmol), and potassium phosphate tribasic (8.43 g, 39.73 mmol) were dissolved in 1,4-dioxane (40 mL) and water (15 mL) and bubbled with nitrogen for 20 min. Then tetrakis(triphenylphosphine)palladium(0) (1.77 g, 1.53 mmol) was added to the reaction mixture, which was stirred for 6 h at 105 °C. After cooling to room temperature, water was poured into the reaction mixture and the solid formed by pouring water was retained by a silica filter. This crude product mixture was extracted with dichloromethane. The organic solution was dried using anhydrous magnesium sulfate and evaporation. After evaporation, the product was purified by column chromatography using hexane and ethyl acetate (Yield: 6.7 g, 87%). $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 8.65 (d, $J$ = 8.7 Hz, 1H).
1 H), 8.58 (d, J = 5.4 Hz, 1 H), 7.97 (d, J = 7.8 Hz, 1 H), 7.90 (s, 1 H), 7.81-7.79 (m, J = 16.2 Hz, 1 H), 7.73-7.71 (m, J = 8.4 Hz, 1 H), 7.68 (d, J = 5.7 Hz, 1 H), 7.56 (d, J = 5.4 Hz, 1 H), 7.42 (d, J = 5.1 Hz, 1 H). 13C NMR (500 MHz, CDCl3): δ (ppm) = 153.38, 144.67, 142.06, 141.00, 139.56, 137.21, 130.26, 128.30, 127.91, 127.36, 126.65, 126.10, 121.24, 120.10, 119.78. HRMS-ESI+ (m/z): [M]+ calcd for C15H9NS2, 267.0176; found, 267.0177.

**Synthesis of Ir(III) dimer [(ttiq)2Ir(μ-Cl)]2 (3):** Ligand, 1-(thieno[3,2-b]thiophen-2-yl)isoquinolone (1.6 g, 5.98 mmol) and iridium(III) chloride hydrate (0.8 g, 2.72 mmol) were dissolved in 2-ethoxyethanol (20 mL) and water (8 mL). The reaction mixture was refluxed overnight under N2 gas. After cooling to room temperature, the black purple precipitate was filtered and thoroughly washed with diethyl ether. The obtained crude dimer product was used without any further purification.

**Synthesis of (ttiq)2Ir(tmd) (4):** Ir(III) dimer [(ttiq)2Ir(μ-Cl)]2 (1 g, 0.66 mmol), 2,2,6,6-tetramethyl-3,5-heptanedione (0.6 g, 3.29 mmol) and sodium carbonate (0.70 g, 6.58 mmol) were dissolved in 2-ethoxyethanol (50 mL). The reaction mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into water and the filtered solid was extracted with dichloromethane. The organic solution was dried using anhydrous magnesium sulfate and evaporation. After evaporation, the black-purple product was purified by recrystallization (Yield: 0.4 g, 67%). 1H NMR (300 MHz, CD2Cl2, d2): δ (ppm) = 8.86-8.82 (m, J = 9.9 Hz, 2 H), 8.30 (d, J = 6.3 Hz, 2 H), 8.01-7.98 (m, J = 9.3 Hz, 2 H), 7.80-7.77 (m, J = 9.6, 4 H), 7.18-7.13 (m, J = 13.5 Hz, 4 H), 5.69 (s, 1 H), 0.94 (s, 18 H). 13C NMR (500 MHz, CDCl3): δ (ppm) = 194.63, 166.90, 148.51, 147.68, 143.55, 142.04, 137.21, 136.12, 131.03, 127.26, 127.07, 126.96, 124.28, 119.02, 115.90, 90.14, 41.10, 28.13. HRMS-FAB+ (m/z): [M+H]+ calcd for C41H35IrN2O2S4, 908.1211; found, 908.1232.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of interests

The authors declare no conflict of interest.

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Figures

Figure 1. Chemical structure of Ir(III) complex [Ir(ttiq)₂tmd].

Scheme 1. Synthetic scheme of cyclometalating ligand and iridium complex.
Figure 2. UV-vis absorbance and PL spectrum of Ir(ttiq)$_2$tmmd a) in solution (blue line: 77 K, red line: 298 K), b) in vacuum-deposited thin-film at room temperature (298 K).
Figure 3. Electrical properties of each device: a) Current density as voltage, b) Radiant emittance as voltage, c) EQE as luminance, and d) Normalized EL spectra of DR/NIR OLEDs.
Figure 4. Operating lifetime of DR/NIR OLED in a) Device 1, b) Device 2, and c) Device 3 at each radiant emittance.
Figure 5. a) Maximum EQE, b) Maximum Radiant Emittance, c) Turn-on voltage of reported DR/NIR OLEDs based on Ir(III) complex. The numerical codes are the same as in the reference article; some missing numbers in (c) are due to a lack of data in the original article. d) Image of working DR/NIR OLED at high radiant emittance.
Figure 6. Cell effect in normal human fibroblasts when irradiating Ir(III)-based DR/NIR OLED (* indicates $P \leq 0.05$ and ** indicates $P \leq 0.01$), values are the mean percentage ± standard error of the mean (n=8) for a) Cell viability and b) Cell proliferation.
### Table 1. Photophysical properties of Ir(ttiq)$_2$tmd

| $\lambda_{abs}$ [nm] | PL [nm] | $\phi_p$ | $\tau_{rad}$ [\(\mu\)s] | $k_r$ [10$^5$ s$^{-1}$] | $k_{nr}$ [10$^5$ s$^{-1}$] | HOMO / LUMO [eV] |
|---------------------|---------|----------|-----------------|----------------|----------------|----------------|
| 536$^a$ / 350$^b$ | 704$^c$ / 690$^d$ / 696$^e$ | 0.15$^f$ / 0.24$^g$ | 0.66$^b$ | 2.27$^i$ | 12.9$^i$ | -4.95$^k$ / -2.82$^l$ |

$^a$UV-vis in CH$_2$Cl$_2$ solution, $^b$UV-vis in vacuum-deposited thin-film, $^c$Maximum peak in THF at 77 K, $^d$Maximum peak in CH$_2$Cl$_2$ at RT (298 K), $^e$Maximum PL peak in vacuum-deposited thin-film at RT (298 K), $^f$PLQY measured in degassed DCM ($\lambda_{ex}$ = 530 nm), $^g$PLQY measured in thin-film (30 nm, $\lambda_{ex}$ = 280 nm), $^h$Radiative lifetime measured in DCM, $^i$k$_r$ = $\phi_p / \tau_{rad}$, $^j$k$_{nr}$ = (1 - $\phi_p$) / $\tau_{rad}$, $^k$Parameter measured using electrochemical CV method, $^l$Parameter calculated through $E_g$ and HOMO level.
**Deep Red to Near-infrared** organic light-emitting diodes based on a novel Ir complex are fabricated with different host materials and structures, and the best device presents high radiant emittance (> 5 mW cm\(^2\)) at low driving voltage.

**New, Reliable Thienothiophenyl-isoquinoline Iridium complex-based Deep Red to Near-Infrared Organic Light-Emitting Diodes with Low Driving Voltage and High Radiant Emittance for Practical Biomedical Applications**