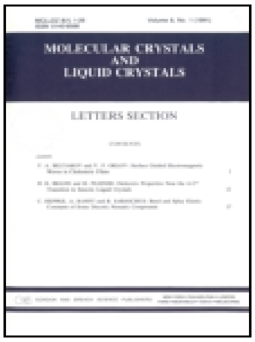

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ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Thota Giridhar, Woosum Cho, Yeong-Soon Gal, Jae Wook Lee & Sung-Ho Jin (2015) Synthesis and Characterization of New Phosphorescent Heteroleptic Iridium (III) Complex by Using Tetrazole as an Ancillary Ligand for Organic Light-Emitting Diodes, Molecular Crystals and Liquid Crystals, 621:1, 17-25, DOI: 10.1080/15421406.2015.1095788

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1095788

Mol. Cryst. Liq. Cryst., Vol. 621: pp. 17–25, 2015
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ISSN: 1542-1406 print/1563-5287 online
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Synthesis and Characterization of New Phosphorescent Heteroleptic Iridium (III) Complex by Using Tetrazole as an Ancillary Ligand for Organic Light-Emitting Diodes

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The yellow emitting tetrazole based heteroleptic iridium(III) complex, bis (diphenylquinoline)iridium(pyridyltetrazole) [$(DPQ)_2Ir(PyTz)$], was synthesized and conformed by ^1H-,^{13}C NMR spectral techniques. The purity was also confirmed by HPLC. The thermal, electrochemical, photophysical and electroluminescent properties were intrinsically investigated. The Ir(III) complex is thermally more stable having thermal decomposition temperature (T_d, 5% weight loss) more than 350°C and it shows very high glass transition temperature T_g-233°C. We have followed the easy and cost effective solution process for $(DPQ)_2Ir(PyTz)$ device fabrication and achieved better performance yellow phosphorescent organic light-emitting diodes (PhOLEDs), maximum external quantum efficiency (EQE) of 5.68%, luminance efficiency 12.63 cd/A, and CIE coordinate of (0.56, 0.43).

Keywords Solution process; tetrazole; yellow PhOLEDs; iridium(III) complex

Introduction

The use of phosphorescent materials has been a major revolution to enhance the electroluminescence efficiency due to allow for the simultaneous harvesting of both singlet and triplet excitons [1]. For getting this phosphorescent materials mainly used third row transition metal complexes, particularly cyclometalated iridium(III) based complexes have been actively studied [2]. In cyclometalated Ir(III) complexes the main advantage is to tune the emission color throughout the visible region by different type of main ligands and ancillary

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ligands [3]. The high quantum yields, short triplet lifetimes, and emission wavelength that can be tuned from blue to deep red are the added advantages of these cyclometalated Ir(III) complexes. The cyclometalated Ir(III) complexes are classified in to two types homoleptic encircled by all same type of ligands and heteroleptic surrounded by two main ligands and one ancillary ligand [4].

In the case of heteroleptic Ir(III) complexes, the emitting colour can be tuned mainly by changing the structure of the main ligands, although in some rare cases ancillary ligand has also an ability to tune the colour [5]. The well-known various ancillary ligands used in solution process phosphorescent organic light-emitting diodes (PhOLEDs) are acetylacetone, picolinic acid, picolinic acid N-oxide and 4-Cl-picolinic acid [6]. Solution processes technologies such as spin-coating, inkjet and screen printing, represents good alternative for PhOLEDs fabrication because of their cost competitiveness and ready scalability. Nevertheless, the use of thermal deposition makes the fabrication process relatively complicated, expensive and maximum wastage of the materials. Thus, much attention in the area of solution-processed PhOLEDs has been given to prepare as well as optimization of device architectures.

Particularly, the electron-donating or accepting units in the ligands can tune the color of the emitters. The yellow emitting Ir(III) complexes have appealed more research interest due to their utility in the fabrication of two color emitting component for white OLEDs with blue emitters [7]. In earlier days for preparing white OLEDs people relied on the mixture of either the three primary colors (red, green and blue) or two complementary colors (blue and yellow).

The main research related to quinoline-based compounds is used as a dopant or host materials to produce PhOLEDs with high efficiencies. These compounds have been used due to their higher electron affinities in opto-electronic materials [8]. Additionally, the quinolone compounds possess short phosphorescence life times to suppress triplet–triplet annihilation and stable at high current density, thus improving device quantum efficiencies [9]. The ease of synthetic variation in tetrazole based ancillary ligand containing Ir(III) complexes over that of the normal heteroleptic Ir(III) complexes. Using $(DPQ)_2Ir(PyTz)$ as a dopant, we achieved PhOLEDs that emits in the yellow (CIE coordinates (0.64, 0.34)), very high luminous current efficiency of $\sim$12.63 cd/A and an external quantum efficiency (EQE) of $\sim$5.68%, which is one of the competent current efficiency and EQE of a solution processed yellow-emitting PhOLEDs.

Experimental

All chemicals and reagents were purchased from Aldrich Chemical Co., and it was used without further purification. The 5-(2′-Pyridyl)tetrazole (**2**) is a known compound and it can be prepared easily in single step from commercially available 2-cyanopyridine and sodium azide [10]. The compound **3** was synthesized according to the method in our previous reports [11]. The UV-visible absorption and the fluorescence spectra were recorded with a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature, respectively. High resolution mass spectra were obtained from the Korea Basic Science and Institute, Daegu Center (HR-ESI Mass). TGA and DSC thermograms were obtained with Mettler Toledo TGA/SDTA 851e and DSC 822e analyzer under an N_2 atmosphere at a heating rate of 10 °C/min, respectively. ^{1}H- and ^{13}C- NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. CV measurements were performed with a CHI 600C potentiostat (CH Instruments), which is equipped with a platinum disc as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl as the reference electrode, at a scan rate of 100 mV s^{-1} using anhydrous MC and 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) as the solvent and electrolyte, respectively. All electrochemical experiments were carried out at room temperature. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc^+). It was assumed that the redox potential of Fc/Fc^+ had an absolute energy level of -4.8 eV under vacuum.

Synthesis of bis[2,4-diphenylquinoline]iridium(III) [5-(2′-pyridyl)tetrazolate]

The cyclometalated Ir(III) μ-chloro-bridged dimer (**2**) (0.50 g, 0.32 mmol) was placed in a flask and dispersed in dichloromethane and ethanol. 5-(2′-Pyridyl)tetrazole (0.23 g, 1.60 mmol) was added to the solution, and the mixture was stirred at room temperature for 8 h. After completion of the reaction crude product was washed with deionized water and extracted with dichloromethane. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using EA/MC/hexane (2:3:5 v/v) as an eluent to give orange solid (0.28 g, 54%). ^{1}H- NMR (300 MHz, $CDCl_3$): δ (ppm): 8.11-7.91 (m, 7H), 7.74-7.67 (m, 3H), 7.56 (s, 10H), 7.41-7.39 (d, 1H), 7.26-7.04 (m, 6H), 6.95-6.75 (m, 4H), 6.64-6.62 (d, 1H). ^{13}C-NMR ($CDCl_3$): δ 170.4, 169.3, 163.0, 154.6, 151.4, 151.0, 149.7, 148.5, 147.9, 147.7, 147.5, 146.9, 138.5, 137.4, 136.2, 134.6, 131.5, 130.5, 130.1, 129.9, 129.8, 129.5, 129.3, 129.1, 129.0, 128.9, 127.8, 127.3, 126.9, 126.5, 126.1, 125.8, 125.2, 122.5, 122.4, 117.9, 117.3. HRESI-MS $[M+H]^+$: m/z calcd for 899.05, found 899.05.

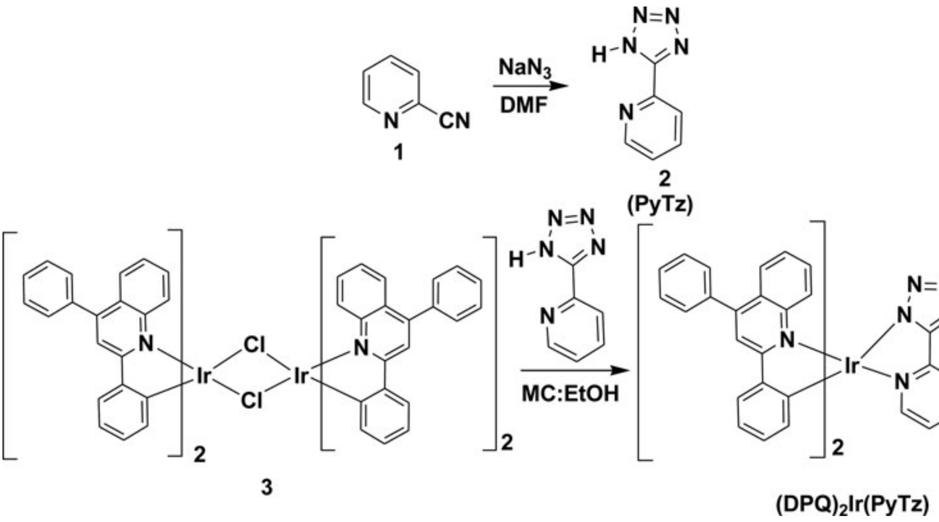
PhOLEDs Fabrication and Measurements

The indium tin oxide (ITO) was coated onto the glass substrate (20 Ω/squre and 110 nm). The ITO glass was UV-ozone treated for 20 min, the PEDOT:PSS ((polyethylenedioxythiophene)-polystyrenesulfonate (H.C.Starck, Clevios P VP AI4083)) was spin-cast onto the substrate and immediately baked at 150 °C for 20 min on a hot plate in air condition. The emitting layer solutions composed of dopant and PVK:PBD:SPPO1 (40:40:20 or 50:30:20) blends in chlorobenzene were spin coated on top of the PEDOT:PSS in a glove box and annealed at 80 °C for 30 min. Then, Bphene (20 nm), LiF (1 nm) and Al (100 nm) were thermally deposited under high vacuum ($< 5.0 \times 10^{-6}$ Torr). The film thickness was measured with α-Step IQ surface profiler (KLA Tencor, SanJose, CA). To characterize the performance of PhOLEDs, the current density-voltage-luminance (J-V-L) characteristic were measured by using a current/voltage source meter (Keithley 236) and an optical power meter (CS-1000).

Results and Discussion

The target heteroleptic yellow emitting $(DPQ)_2Ir(PyTz)$ was synthesized according to the synthetic route as shown in Scheme 1. The ancillary ligand 5-(2′-Pyridyl)tetrazole is a known compound and it can be prepared easily in single step from commercially available 2-cyanopyridine and sodium azide and the compound **2** was synthesized according to the previous report. The compound **2** can be easily converted to heteroleptic Ir(III) complex by simple approach rather than sophisticated and high temperature reaction conditions.

The ligand and Ir(III) complex are readily soluble in common organic solvents suchlike methylene chloride (MC), chloroform (CF), and ethylacetate (EA), etc. The chemical structure of the Ir(III) complexes were confirmed by the ^{1}H-, ^{13}C-NMR and HR-ESI mass spectral techniques.



Scheme 1. Synthesis of Ir(III) complex.

The excellent thermal stability (T_d) with high T_g values allows the preparation of homogeneous and stable amorphous thin films which is critical factor for the operation of solution processing PhOLEDs. The thermal stability of $(DPQ)_2Ir(PyTz)$ was identified by thermo gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis under N_2 atmosphere at a heating rate of 10 °C/min. The thermal decomposition temperature (T_d) of $(DPQ)_2Ir(PyTz)$ at 5% mass loss ($\Delta T_{5\%}$) was 354 °C and the glass transition temperature (T_g) was 233 °C, respectively. This indicates $(DPQ)_2Ir(PyTz)$ has good thermal stability for evaluation high temperature device studies.

The photophysical properties of $(DPQ)_2Ir(PyTz)$ were measured using UV–visible absorption and photoluminescence (PL) spectra at room temperature in CF solution. The four absorption maxima of the Ir(III) complex show in the range of 291-496 nm. The higher energy region below 350 nm absorption bands are corresponding to the spin-allowed $^{1}\pi$-π^{*} transitions of the cyclometalated ligands. The singlet metal-to-ligand charge-transitions (^{1}MLCT), ^{3}MLCT and $^{3}\pi$-π^{*} weak spin forbidden absorption bands are located at lower energy region 400-456 nm. Additionally, the $(DPQ)_2Ir(PyTz)$ showed a PL emission maximum at 578 nm in CF solution. When compared with the other ancillary ligands like picolinic acid and acetylacetone [$(DPQ)_2Ir$(pic-N-O) and $(DPQ)_2Ir(acac)$] the 5-(2′-Pyridyl)tetrazole ancillary ligand shows little hypsochromic shift in PL maxima due to non-uniform electron density in tetrazole ring.

The electrochemical properties of the $(DPQ)_2Ir(PyTz)$ were studied by cyclic voltametry (CV) analysis. The onset oxidation potential is located at 1.10 V and the corresponding highest occupied molecular orbital (HOMO) energy level was found to be -5.48 eV and the reduction potential located at −1.52 V and the corresponding lowest unoccupied molecular orbital (LUMO) was found −2.76 eV with ferrocene/ferrocenium as a reference redox system (4.8 eV below vacuum). The Ir(III) complex showed reversible redox waves over

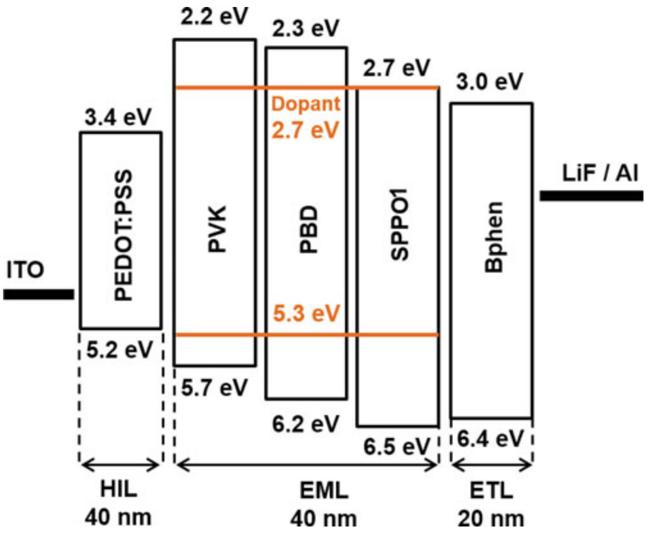


Figure 1. Energy level diagram of the materials.

both the anodic and cathodic ranges. Hence, it suggests that the stable Ir(II) and Ir(IV) radicals are formed.

To investigate the EL properties of solution-processed PhOLEDs using $(DPQ)_2Ir(PyTz)$ fabricated with the following four configuration devices I, II: ITO/PEDOT:PSS/PVK (40 wt%):PBD (40 wt%):SPPO1 (20 wt%):$(DPQ)_2Ir(PyTz)$ (8 wt%, device I), (5 wt%, device II)/Bphen/LiF (1 nm)/Al (100 nm); devices III, IV: ITO/PEDOT:PSS/PVK (50 wt%):PBD (30 wt%):SPPO1 (20 wt%):$(DPQ)_2Ir(PyTz)$ (8 wt%, device III), (5 wt%, device IV)/Bphen/LiF (1 nm)/Al (100 nm). Generally, it is necessary to select a suitable host for efficient energy transfer and/or charge trapping from the host to the phosphorescent dopant and to avoid concentration quenching to maximize the performance of PhOLEDs. One of the most commonly used polymers in PhOLEDs is poly(N-vinylcarbazole) (PVK) due to its excellent film-forming properties, wide band gap, high glass transition temperature, and good hole mobility at typical electrical fields. In this work, we have used $(DPQ)_2Ir(PyTz)$ into a host polymer matrix of PVK blended with an electron-transport material, 2-(4-biphenyllyl-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) (PBD).

The device configuration with the HOMO and LUMO energy levels were calculated from electrochemical measurements and showed in Figure 1. The energy band gap of $(DPQ)_2Ir(PyTz)$ at 2.6 eV, HOMO 5.3 eV, and LUMO 2.7 eV are between the HOMO and LUMO energy levels of PVK:PBD:SPPO1, suggesting that dopant can possibly trap both electrons and holes in PhOLEDs with the device configuration. In view of the HOMO and LUMO energy levels of PVK and PBD, we attempted to use them as the host- and electron-transporting materials in the fabrication of PhOLEDs because of their good hole- and electron transporting ability. These energy band diagrams indicated that the HOMO and LUMO of PVK is little higher than that of PBD and SPPO1 indicates that the efficient hole and electron transportation can occur in right direction. This good alignment of energy level is important to facilitate carrier injection into both the transport molecules and $(DPQ)_2Ir(PyTz)$.

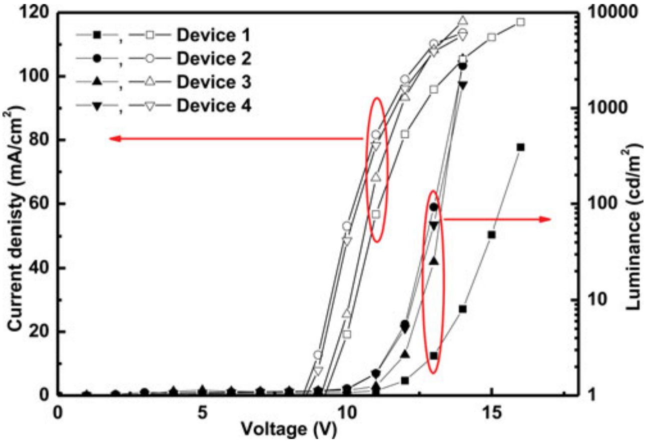


Figure 2. Current density-voltage-luminance (J-V-L) characteristics of $(DPQ)_2Ir(PyTz)$.

The current density–voltage–luminance (J–V–L) characteristics of $(DPQ)_2Ir(PyTz)$ was investigated in different doping concentration of dopant as well as different ratios of hole transporting materials (HTM) and shown in Figure 2 and Figure 3 and the values are depicted in Table 1. However, the dopant at 8% weight ratio performances of PhOLEDs is better than 5% weight ratio. We found that the performances of PhOLEDs not improved as the concentration of carrier-transporting material increased but the performances gradually decreased if the percentage of weight decreases. We expected that there should be an efficient exothermic energy transfer from the host triplet state to the Ir(III) complexes triplet state within the emitting layer due to an excellent triplet energy confinement on the Ir(III) complexes.

Moreover, the SPPO1 serves as carrier block/electron transporting layer effectively enable electron injection/transport and charge carrier balance within the emitting layer. The LUMO energy of Ir(III) complex is close to the electron transport layer (ETL) SPPO1, an

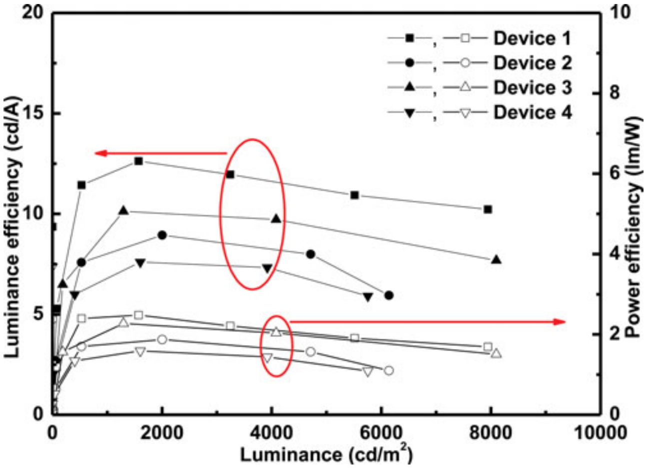


Figure 3. Luminance efficiency-luminance-power efficiency characteristics of $(DPQ)_2Ir(PyTz)$.

Table 1. Performance parameters of $(DPQ)_2Ir(PyTz)$

	Voltage (V)	Luminance (cd/m^2)	EL$_{max}$ (nm)	E.Q.E (%)		Luminance efficiency (cd/A)		Power efficiency (lm/W)	
	Turn-on	Max.	At 10 mA/cm^2	Max.	At 1000 cd/m^2	Max.	At 50 mA/cm^2	Max.	At 50 mA/cm^2
Device 1	9.12	7945	585	5.68	5.39	12.63	10.93	2.48	1.91
Device 2	8.49	6141	585	4.05	3.60	8.94	7.99	1.87	1.57
Device 3	9.05	8099	583	4.41	4.01	10.13	9.72	2.27	2.04
Device 4	8.59	5756	585	3.45	3.09	7.60	7.33	1.59	1.44

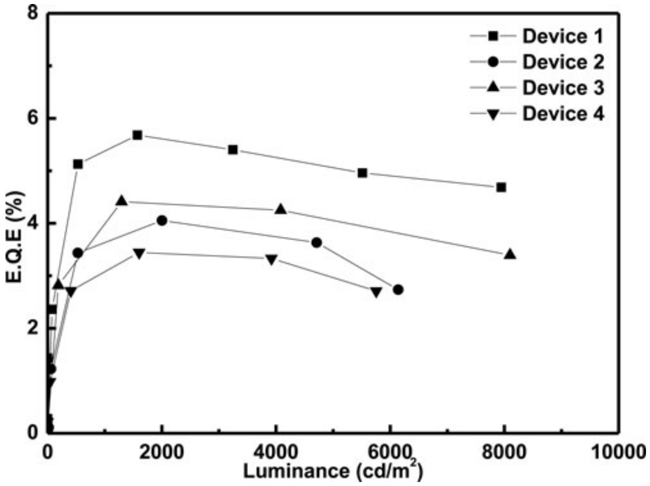


Figure 4. External quantum efficiency (E.Q.E) characteristics of $(DPQ)_2Ir(PyTz)$.

important feature that ensures efficient electron injection into both the transport molecules and the Ir(III) complexes. Additionally the SPPO1 layer acts as a hole blocking layer to prevent frequent consignment of holes. The maximum EL emission peaks of $(DPQ)_2Ir(PyTz)$ is observed at 585 nm, the shift of the exciton recombination zones, the EL spectra of PhOLEDs display a greater 7 nm red shift than those seen in the PL spectra. The maximum luminance of PhOLEDs using $(DPQ)_2Ir(PyTz)$ is 12.63 cd/A and EQE of 5.68% as shown in Figure 4 with the CIE coordinates of (0.64, 0.34).

Conclusions

We designed and synthesized phenyl-quinoline and 2-pyridyltetrazole based heteroleptic Ir(III) complex, [(DPQ)2Ir(PyTz)], as a yellow emitter for OLEDs. It was synthesized using simple approach rather than using sophisticated and high temperature reaction conditions. Due to the introduction of 2-pyridyltetrazole as ancillary ligand, the color and perturbation of electron density was altered significantly. Thus, $(DPQ)_2Ir(PyTz)$ complex was shown external quantum efficiency of 5.68% with CIE coordinates of (0.56, 0.43) and can use as a key color component for fabricating white PhOLED.

Acknowledgments

This work was supported by a grant from the National Research Foundation of Korea (NRF) of the Ministry of Science, ICT & Future Planning (MSIP) of Korea (NRF-2011-0028320) and the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT & Future Planning (MSIP) of Korea (NRF-2013M3C1A3065522).

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