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Preparation of Blue-Emitting Phosphorescent Iridium(III) Complex Under Ultrasound Reaction

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F_2MeIrpic (Iridium(III)bis[2-(2′,4′-difluorophenyl)-4-methyl pyridinato-N,$C^{2'}$] picolinate) was synthesized to develop a blue-emitting phosphorescent Ir(III) complex. The synthesized F_2MeIrpic showed sky blue light with the maximum PL peak at 470 nm. Generally the reaction time and maximum yield of F_2MeIrpic were known to be 78 hours and 28%, respectively. The reaction is composed of three steps which are the synthesis of ligand (F_2Meppy), Ir-dimer and F_2MeIrpic with Ir-dimer and picolinic acid. The synthesis of F_2MeIrpic is a rate determining step. The solubility and dispersibility of Ir-dimer in solvent are important reaction parameters which determine reaction time and yield, because Ir-dimer is not soluble in almost all solvent. Among various solvents Tetrahydrofuran(THF) was the best solvent to solve Ir-dimer. Ir-dimer was dispersed well by an ultra-sonication in the solvent during reaction. The reaction time was reduced to 36 hours and yield was enhanced to 45% by ultra sound in THF.

Keywords: blue-emitting; Iridium(III); organic light-emitting diode; phosphorescent material; ultrasound

INTRODUCTION

Blue emission in the organic light-emitting device (OLED) is an important key in the full-color flat-panel displays, because blue is one of three primary colors [1]. The main obstacle to its application in displays or monitors is still their lack of stability and efficiency [2]. One of the key developments in sciences and technology for efficiency of OLED is the discovery of electro phosphorescence which lifts the upper

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limit of the internal quantum efficiency of the usual fluorescent dopant-based devices from 25% to nearly 100%. Phosphorescence is inherently a slower and less efficient process, but triplet states constitute the majority of electro generated excited states (75%), so the successful utilization of the triplet manifold to produce light should undoubtedly increase the overall luminance [3]. Princeton University group and Southern California group have demonstrated a way to break through this efficiency limitation by using certain organic materials which emit intense phosphorescence from triplet states at room temperature [4].

Synthesis of heavy metal complexes such as Ir(III) [5,6,7,8] and Pt(II) [9] complexes, which are used as phosphorescent dopants, has a great attention because of their potential applications in the organic light emitting devices (OLEDs) [12]. Among the complexes, F_2Iracac and F_2Irpic ($F_2 = 2$-(20, 40-difluorophenyl) pyridine; acacH = 2,4-pentanedione; picH = 2-picolinic acid) [5] are good examples for phosphorescent blue-emitting materials.

Recently, F_2MeIrpic (Iridium(III)bis[2-(2′,4′-difluorophenyl)-4-methyl pyridinato-N,$C^{2'}$]picolinate) which shows sky blue light with the maximum PL peak at 470 nm was synthesized for phosphorescent dopant [10]. It was reported that the reaction time and maximum yield of F_2MeIrpic were generally long reaction time of 78 hours and poor yield of 28%, respectively [10]. Especially in the synthesis of iridium based metal complex, general precursor, $IrCl_3 \cdot 3H_2O$ and Ir-dimmer are poor soluble and not dispersed in most of solvents. So those are reasons of long reaction time and poor yield. As we know the ultrasound chemical reactions are very efficient mixing methods for high yields and short reaction times in many different types of organic reactions compared with conventional methods [11].

In this paper we report a preparation of F_2MeIrpic under ultrasound condition and compare it with conventional method [10]. The effect of the ultrasound and other reaction conditions were investigated to obtain the optimum reaction conditions for the preparation of F_2MeIrpic.

EXPERIMENTAL

Experimental Setup

The experimental setup for the preparation of F_2MeIrpic under ultrasound condition is shown schematically in Figure 1. Volume of flask reactor was 250 ml and reactor was made by Pyrex glass. The reactor is placed in silicon oil batch and ultrasound reached to reactants through silicon oil.

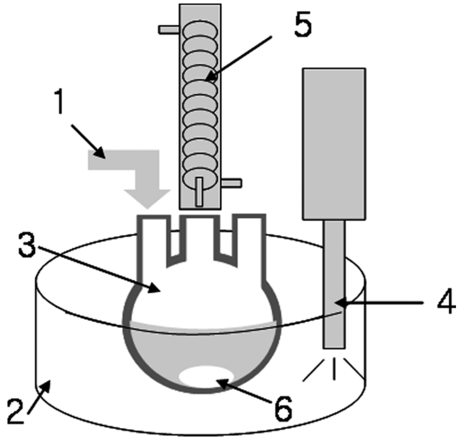


FIGURE 1 Diagram of flask reactor assisted by ultrasound : (1) N_2 purging; (2) thermostatic bath; (3) flask reactor; (4) ultrasonic probe; (5) condenser; (6) magnetic bar.

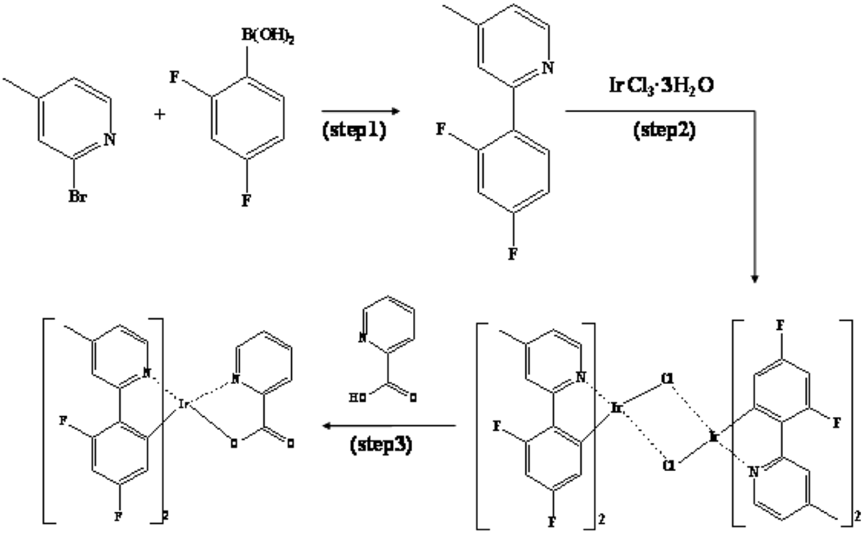
Synthesis

2-[2,4-difluorophenyl]-4-methylpyridine, $[(F_2Meppy)_2IrCl]_2$ and F_2MeIrpic were prepared by the following methods described in the literature [10,12]. The synthetic routes of the ligands and the complexes consist of three steps as shown in Scheme 1. The reactions were operated under conventional and ultrasound condition.

Synthesis of F_2Meppy, (2-[2,4-difluorophenyl]-4-methylpyridine) (Step 1)

10 mmol of 2-chloro-4-methyl pyridine, 12 mmol of 2,4-difluorophenylboronic acid, and 1 mmol of triphenylphosphine were dissolved in 1,2-dimethoxyethane (50 ml). 50 ml of 2 M K_2 CO_3 aqueous solution was added and the mixture was purged with nitrogen gas. 0.25 g of palladium acetate was added and the mixture was refluxed for 18 h. The two phases were then separated and the aqueous phase was extracted with ethyl acetate. The combined organic phases were washed with water and brine, successively. After evaporation of the solvent, the pure product was obtained by column chromatography.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: 8.51 (d, $J = 5.7$ Hz, 1H), 7.98 (m, 1H), 7.26 (t, $J = 2.1$ Hz, 1H), 6.94 (m, 2H), 6.78 (dd, $J = 2.4$, 5.7 Hz, 1H), 3.87 (s, 3H).



SCHEME 1 The reaction route for the synthesis of F_2MeIrpic.

Synthesis of Ir-dimer, ([(F_2Meppy)$_2$IrCl]$_2$) (Step 2)

A solution of $IrCl_3 \cdot 3H_2O$ (1 mmol) and 2-(2′,4′-difluorophenyl)-4-methylpyridine (3 mmol) in 2-ethoxyethanol (30 ml) was refluxed for 24 h under nitrogen. The pale green mixture was cooled to room temperature and 100 ml of 1 M HCl was added to precipitate the product. The mixture was filtered and washed with 100 ml of 1 M HCl followed by 50 ml of water, and then dried. The product was obtained as a light green powder.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: 8.91 (d, $J = 6.6$ Hz, 4H), 7.80 (s, 4H), 6.43 (m, 4H), 6.31 (t, $J = 9.9$ Hz, 4H), 5.37 (d, $J = 9.0$ Hz, 4H), 4.01 (s, 12H).

Synthesis of F_2MeIrpic, (Iridium(III)bis[2-(2′,4′-difluorophenyl)-4-methyl pyridinato-N,C$^{2'}$]picolinate) (Step 3)

2.2 mmol of picolinic acid was added to a room temperature solution of 0.8 mmol of [(F_2Meppy)$_2$IrCl]$_2$ in 60 ml of THF(Tetrahydrofuran) and 2 mmol Ag($OCOCF_3$) was added. The mixture was heated to reflux under nitrogen in a silicon oil bath for 48 hours. The reaction mixture was cooled to room temperature and the pale yellow precipitate was filtered off. The pure product was obtained by a flash chromatography.

^{1}H NMR (300 MHz, $CDCl_3$): ppm 8.48 (d, $J = 6.9$ Hz, 1H), 8.32 (d, $J = 7.2$ Hz, 1H), 7.92 (t, $J = 6.6$ Hz, 1H), 7.76 (m, 3H), 7.40 (td, $J = 1.5$, 5.7 Hz, 1H), 7.17 (d, $J = 6.6$ Hz, 1H), 6.73 (dd, $J = 2.7$, 6.9 Hz, 1H), 6.53 (dd, $J = 2.7$, 6.6 Hz, 1H), 6.42 (m, 2H), 5.88 (dd, $J = 2.3$, 8.7 Hz, 1H), 5.64 (dd, $J = 2.6$, 8.7 Hz, 1H), 4.06 (s, 6H).

Fabrication and Testing of OLED

30 nm of PEDOT:PSS as the hole transporting layer and 30 nm of the complex doped (7%) PVK as the emitting layer were spin coated sequentially onto 200 nm ITO substrate. In a vacuum chamber at a pressure of 10^{-6} Torr 10 nm of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) as a hole blocking layer, 30 nm of Alq_3 as the electron transport layer; and a cathode composed of 1 nm lithium fluoride and 120 nm aluminum were sequentially deposited onto the spin coated substrate to give the device structure. The current – voltage (I–V) profiles and light intensity characteristics for the above-fabricated devices were measured in glove box under nitrogen condition at ambient temperature using a Keithley 2400 Source Meter/2000 Multimeter coupled to a PR 650 Optical Meter.

RESULTS AND DISCUSSION

Optical Properties of F_2MeIrpic and Performance of OLED Device

UV-Vis spectra and PL spectra of F_2MeIrpic under conventional and ultrasound condition were shown in Figures 2 and 3. As shown in Figures 2 and 3, the strong absorption peaks are at 375 and 450 nm and the PL spectrum of synthesized F_2MeIrpic shows emission bands at 468 and 492 nm as same as those of reference [10]. It was clear that no change was carried out on optical properties under ultrasound condition compared with conventional method.

An electroluminescent device was fabricated with structure ITO (200 nm)/PEDOT:PSS (30 nm)/PVK + 7% Ir-compex (30 nm)/BCP (10 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (120 nm). EL device structure is shown in Scheme 2. Figure 4 shows the EL spectrum with a maximum at the peak wavelength of $\lambda_{max} = 484$ nm and additional subpeaks at $\lambda_{sub} = 502$ nm and 540 nm which generally agrees with the PL spectral shape. The device of F_2MeIrpic shows sky blue light because of two additional subpeaks. This device shows a luminance value of 300 cd/m^2 and luminance efficiency of 1.45 cd/A at 20 mA/cm^2 current density

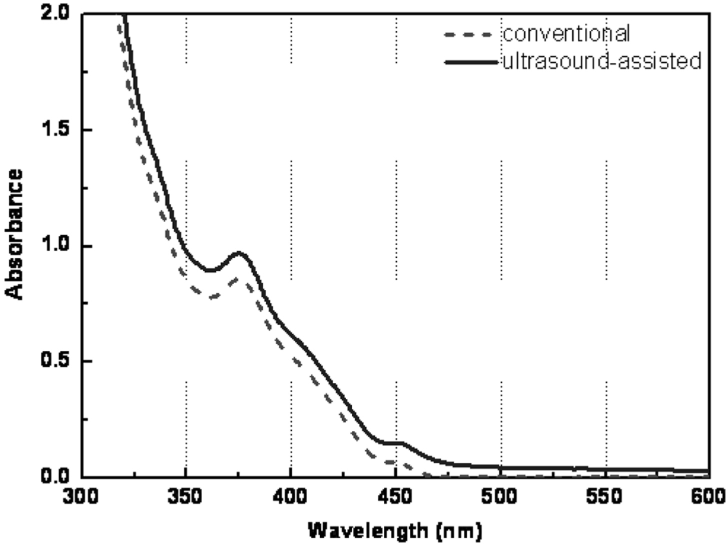


FIGURE 2 UV–Vis absorption spectra for F_2MeIrpic synthesized under conventional and ultrasound condition in CH_2Cl_2.

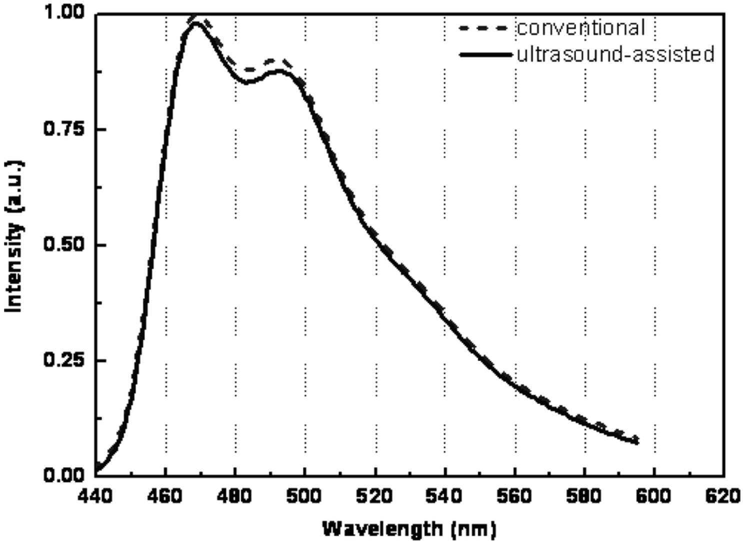
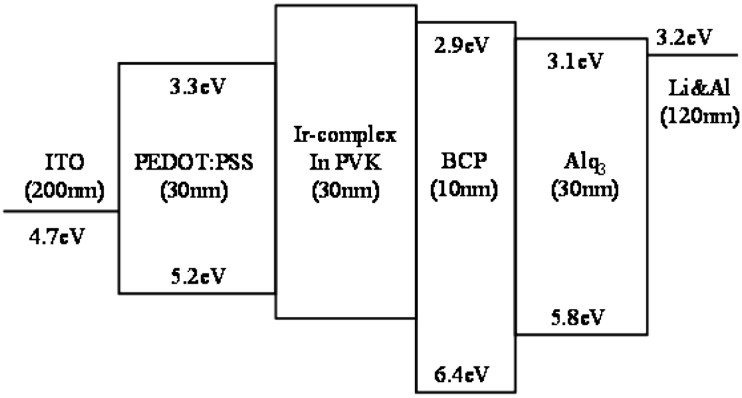


FIGURE 3 Room temperature solution PL spectra for F_2MeIrpic synthesized under conventional and ultrasound condition in CH_2Cl_2.



SCHEME 2 El device structure of F_2MeIrpic.

and 6.4 V voltage. Luminance, current density and luminance efficiency are plotted as functions of voltage and current density in Figures 5 and 6.

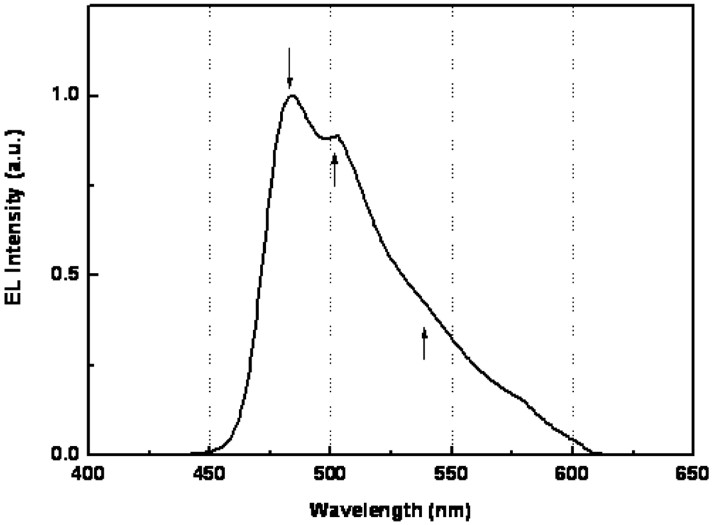


FIGURE 4 Electroluminescence spectra of the following OLED structure: ITO (200 nm)/PEDOT:PSS (30 nm)/PVK + 7% Ir-complex (30 nm)/BCP (10 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (120 nm). The EL spectrum has a maximum at the peak wavelength of $\lambda_{max} = 484$ nm and additional subpeaks at $\lambda_{sub} = 502$ nm and 540 nm which agrees with the PL spectral shape.

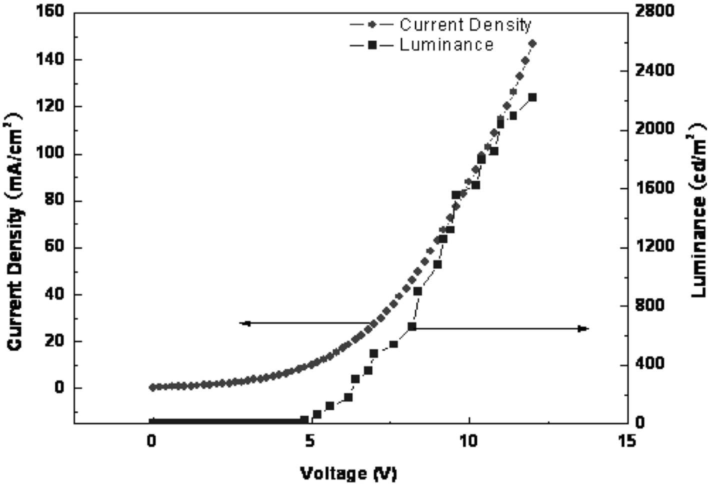


FIGURE 5 Comparative plot of current density, voltage and luminance characteristics for the device.

Effect of Ultrasound

Table 1 shows the reaction yield of each step under ultrasound condition compared with conventional method. The reaction yield

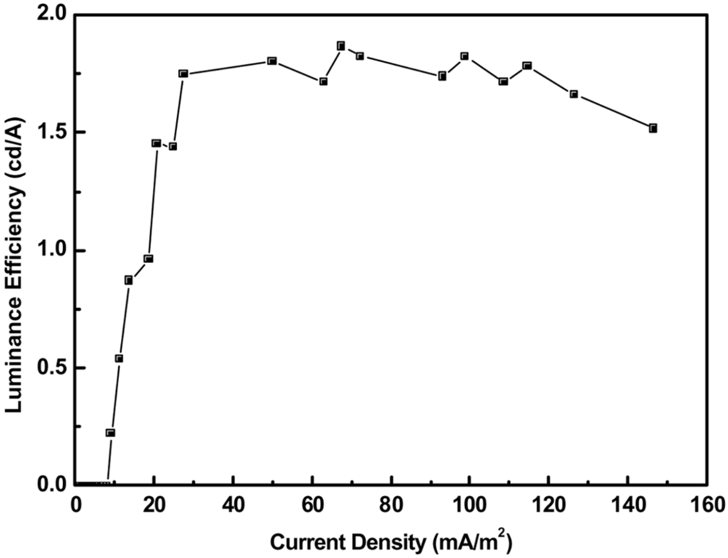


FIGURE 6 Plot of luminescent efficiency vs. current density of device.

TABLE 1 Effect of Ultrasound Condition on Each Reaction Step

Step	Condition	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
1	Ultrasound	70	12	80.1	98.32	78.75
	Conventional	70	18	79.80	94.81	75.65
2	Ultrasound	175	12	79.66	84.32	67.17
	Conventional	175	12	65.66	76.82	43.48
3	Ultrasound	175	12	79.51	93.71	74.50
	Conventional	175	48	52.10	97.83	50.96

was enhanced by using ultrasound. As shown in Table 1, reaction times of step 1 and 3 were shortened by 6 h at same conversion. In addition, the reaction yields of step 2 and 3 were enhanced to 67% and 74%. Figure 7 shows a relationship between conversion of step 1 and reaction time. The maximum conversion of step 1 in Figure 7 is not changed at both conditions, but the reaction time for maximum conversion of step 1 in ultrasound condition is faster than in conventional condition.

A possible reason is that ultrasound can make reactants contact with reaction site and products move out from reaction site fast and

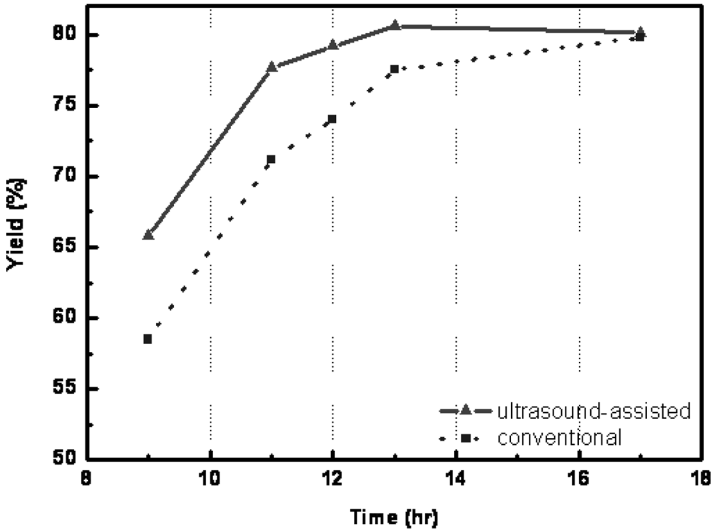


FIGURE 7 Relationship between yield and time under conventional and ultrasound condition in step 1 reaction.

efficiently. Especially for the step 2 and 3 reactions, the reactants of $IrCl_3 \cdot H_2O$ and Ir-dimmer are not soluble in most of the solvents. Ultrasound can help to disperse non-soluble reactants well in solvent and replace product which have already reacted [13]. Another possible explanation is that ultrasound can break iridium-chloride bond more easily and make Ir-dimer produce cation (F_2MeIr^+). Higher yield of step 3 reaction can be obtained by combination of interaction between Ag^+ and Cl^- and ultrasound, because the break of iridium-chloride bond and formation of cation was occurred by only interaction between Ag^+ and Cl^- in conventional method.

Effect of Reaction Temperature

Figure 8 shows a conversion of each reaction step depending on different temperatures. Each reaction reached higher conversion with increase of temperature. This result explains that these reactions are endothermic and the maximum temperatures of each reaction step are 78°C, 176°C and 176°C. These temperatures are boiling points of solvents used.

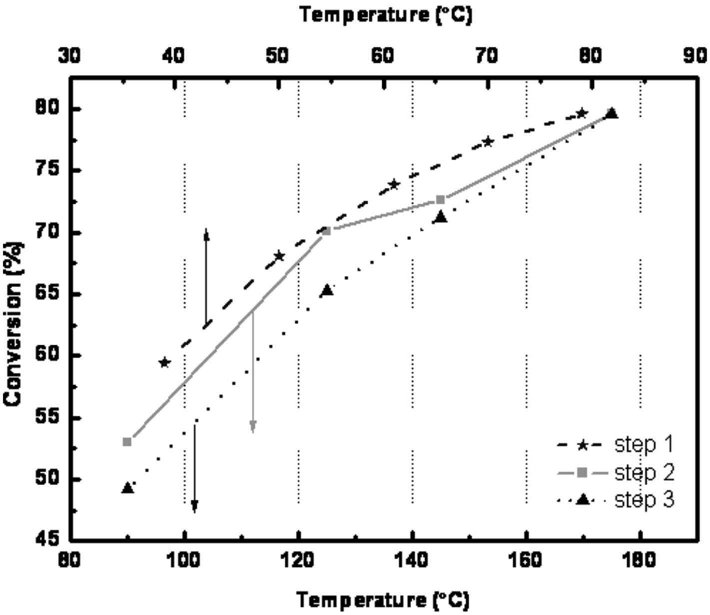


FIGURE 8 Relationship between conversion and reaction temperature in each reaction step.

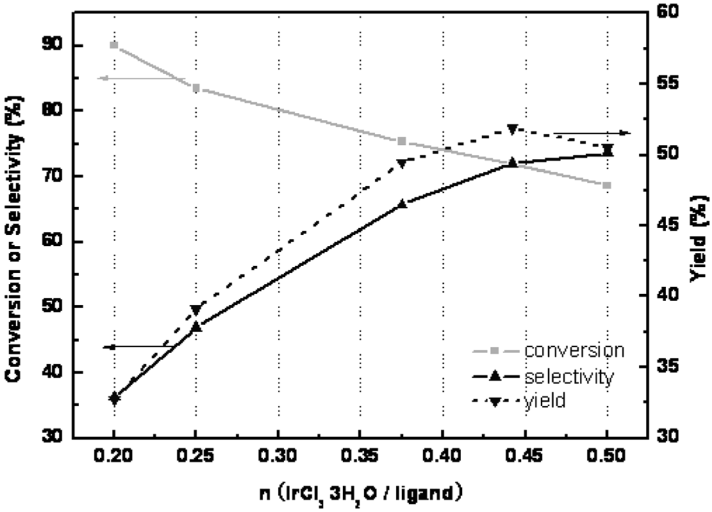


FIGURE 9 Relationship between n $(IrCl_3 \cdot 3H_2O)$/n (F_2Meppy) and conversion or selectivity.

Effect of $IrCl_3 \cdot 3H_2O$ versus F_2Meppy Molar Ratio

For step 2 reaction, an ideal schiometric ratio of $IrCl_3 \cdot 3H_2O$ to F_2Meppy is 1:2. But the n $(IrCl_3 \cdot 3H_2O)$/n (F_2Meppy) is generally reported 0.3 for higher conversion [10]. The influence of n $(IrCl_3 \cdot 3H_2O)$/n (F_2Meppy) on the conversion and selectivity of Ir-dimer under the standard reaction conditions was shown in Figure 9. It was clear that the conversion of $IrCl_3 \cdot 3H_2O$ increased with decreasing n $(IrCl_3 \cdot 3H_2O)$/n (F_2Meppy) ratio from 0.5 to 0.2, whereas the selectivity of Ir-dimer decreased. The yield was 51.9% at 0.44 of n $(IrCl_3 \cdot 3H_2O)$/n (F_2Meppy) and that was maximum yield. Furthermore two reactants of $IrCl_3 \cdot 3H_2O$ and F_2Meppy were too expensive or took much time to prepare generally. These results are expected that the synthesis of Iridium complex under ultrasound reaction is beneficial for research and industry with its good efficiency.

CONCLUSIONS

$F_2MeIrpic$ of sky blue light with the maximum PL peak at 470 nm was synthesized successfully under conventional and ultrasound conditions. EL performance of a fabricated OLED with $F_2MeIrpic$ shows a maximum at the peak wavelength of $\lambda_{max} = 484$ nm and this result is reasonable for a blue emitting phosphorescent material. In the synthesis of F_2MeIrpic, the reaction time and yield are long and poor, because reactants, $IrCl_3 \cdot 3H_2O$ and Ir-dimer, are not soluble in most of solvents. Higher yield was obtained under ultrasound condition. The ultrasound could help to disperse non-soluble reactants well in solvent and replace product which have already reacted. The total reaction yield was enhanced to 45% and the total reaction time was shortened to 36 hours under ultrasound condition. Other optimized operation conditions were the reaction temperatures of 78°C, 176°C, and 176°C, and the molar ratio ($IrCl_3 \cdot 3H_2O/F_2$Meppy) of 0.44.

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