



Stable orange and white electrophosphorescence based on spirobifluorenyltrifluoromethylpyridine iridium complexes



Wenguan Zhang^{a,*}, Chunjun Liang^b, Zhiqun He^b, Hui Pang^a, Yongsheng Wang^{a,b}, Shengmin Zhao^a

^a Lab of Printing & Packaging Material and Technology-Beijing Area Major Laboratory, Beijing Institute of Graphic Communication, Beijing 102600, PR China

^b Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, PR China

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ABSTRACT

Novel complexes bis[2-(9,9'-spirobifluoren-2-yl)-5-trifluoromethylpyridinato-C³, N] iridium (acetylacetonate) (**8**) and bis[2-(9,9'-spirobifluoren-2-yl)-5-trifluoromethylpyridinato-C³, N] iridium (2-picolinic acid) (**9**) were synthesized. Trifluoromethyl group and 2-picolinic acid were incorporated to tune luminescent color and spirobifluorene with supramolecular steric hindrance was introduced to suppress intermolecular interaction. The orange-emissive electrophosphorescent devices for **8** and **9** exhibited stable electroluminescent (EL) peaks at 580 (or 584) and 568 (or 572) nm at the different voltages, and maximum current efficiencies of 21.6 and 35 cd/A. The white-emissive devices of the dual emitting layer based on the orange (**8** or **9**) and blue (FlrPic) phosphor showed CIE coordinates of (0.32, 0.37) and (0.33, 0.39), and maximum current efficiencies of 10.6 and 13.8 cd/A. The CIE coordinates with the increasing of the operating voltage were stable. High efficiency and slow decay of devices indicated that **8** and **9** were highly efficient orange emitters.

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1. Introduction

White organic light-emitting diodes (WOLEDs) have the potential use in display backlight, full color display and solid-state light [1,2]. WOLEDs using phosphorescent materials have significant improvements in efficiency and backlights for full-color active-matrix displays. WOLEDs composed of the three separate emitters from red, green and blue are the most common approach [3,4]. The device structure is simplified further to use the dual-component blue and orange emitters doped in the separate layers in an appropriate ratio [5,6]. The WOLED employs dual emission layers, which are composed of a 5% orange-emissive iridium complex [Ir(L)₃] (HL = (9,9-diethyl-7-pyridinylfluoren-2-yl) diphenylamine) doped in 4',N,N'-dicarbazolebiphenyl (CBP) and a 8% blue-emitting bis(4,6-difluorophenyl) pyridinato-N,C²) picolinato iridium (FlrPic) in doped N,N'-dicarbazolyl-3,5-benzene (mCP). The two emissive layers are formed by co-deposition of dopant and host. The electroluminescence (EL) spectra are dependent on the operating voltage strongly. The Commission Internationale de

L'Eclairage (CIE) coordinates are (0.31, 0.41), the color purity is expected to be improved [7].

In order to achieve high-efficiency WOLEDs, efficient orange-emitting iridium complex phosphors are explored. Fluorination is an effective way to improve electron mobility, thermal stability [8] and volatility [9] of organometallic complexes. The (naph) ligand is modified by incorporating a trifluoromethyl group on the pyridine ring to generate a larger bathochromic effect on the emission wavelength of the corresponding Ir complexes [10]. Introducing supramolecular steric hindrance (SSH) is an important strategy to control host-guest or dopant-dopant interactions, while orthogonally bulky spirobifluorene (SPF) and its analog [11] exhibit SSH effect on the performance of phosphorescent organic light-emitting diodes (OLEDs). Spiro-functionalized tris[2-(9,9'-spirobifluoren-2-yl) pyridinato-C³N₃] iridium (III) (fac-Ir(SFP)₃) shows high quantum yield, morphological stability and performance of devices [12]. The emissions of Ir complexes, in which acetylacetonate (acacH) is replaced by 2-picolinic acid (picH) with high triplet energy and electron-deficiency structure as L' ligand, are blue-shift and efficient [13].

In our previous work, the fluorene as the extent of conjugation was introduced to the 2-position of pyridine with a trifluoromethyl group. The ligand 2-(9,9-diethylfluoren-2-yl)-5-trifluoromethylpyridine (fl-5CF₃-py), two complexes (fl-5CF₃-py)₂Ir(acac) and (fl-

* Corresponding author: Fax: +86 10 60261108.

E-mail address: wenguanzhang@sina.com (W. Zhang).

5CF₃-py)₂Ir(pic) [14] were reported, the organic light-emitting devices were characterized. In this paper, the orthogonally bulky spirobifluorene as a π–π stacking supramolecular steric hindrance (SSH) model was incorporated into the 2-position of pyridine with a trifluoromethyl group. A novel ligand 2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridine (sfp-5CF₃-py), two complexes (sfp-5CF₃-py)₂Ir(acac) (**8**) and (sfp-5CF₃-py)₂Ir(pic) (**9**) were synthesized, respectively. The trifluoromethyl group influenced electron extent of delocation between pyridyl and spirobifluorene-2-yl rings, while electron-deficiency 2-picolinic acid altered the ³MLCT excited state of complex, which tuned luminescent color. The orange and white phosphorescent organic light-emitting devices (OLED) based on **8** or **9** as a dopant were fabricated and characterized.

2. Experimental

2.1. Materials and instruments

Fluorene, 2-chloro-5-trifluoromethylpyridine, Pd(OAc)₂, Cs₂CO₃, IrCl₃·nH₂O, PPh₃, *n*-butyllithium (1.6 mol/L) and 2-picolinic acid were purchased from Acros Organics. Chemicals and solvents were used as received in the highest commercially available grade unless described otherwise. Dioxane and tetrahydrofuran (THF) were refluxed with sodium and benzophenone, and purified with distillation. 2-Methoxyethanol was purified through distillation at a reduced pressure. The synthesized compounds were characterized using elemental analysis (Carlo Erba 1106), ¹H NMR spectroscopy (Bruker Avance 400), and mass spectrometry analysis (Shimadzu LC-MS2010A), respectively. Cyclic voltammetry (CV) analyses were carried out by using Zahner Zennium. The measurement was performed in an anhydrous dichloromethane solution with the presence of *tetra-n*-butylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as supporting electrolyte. A Hg/Hg₂Cl₂ electrode was used as the reference electrode, a glass carbon rod as the working electrode and a platinum wire as the counter electrode. Ferrocene was chosen as a reference material at a scan rate of 50 mV s⁻¹. The UV–vis absorption spectrum was measured by using GBC Cintra 303 Spectrometer. Photoluminescent (PL) spectrum was recorded with PerkinElmer LS-55 luminescence spectrometer. Phosphorescence quantum yield (Φ) was measured against the reference fac-Ir(ppy)₃ (Φ_{fac-Ir(ppy)₃} = 0.4) in Ar-saturated toluene (10⁻⁵ M) at 298 K.

2.2. Synthetic procedures

2-Bromofluorene (**1**) [15], 2-bromofluorenone (**2**) [16,17], 2-bromo-9,9'-spirobifluorene (**4**) [18,19] and 9,9'-spirobifluorenyl-2-boronic acid (**5**) [20] were prepared as described in corresponding references, respectively.

2.2.1. 2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridine (sfp-5CF₃-py) (**6**) [10,14]

Pd(OAc)₂ (0.105 g, 0.467 mmol), PPh₃ (0.495 g, 1.88 mmol) and dioxane (20 ml) were charged in a three-neck round bottomed flask under N₂ atmosphere, and stirred for 30 min at room temperature. 2-Chloro-5-trifluoromethylpyridine (1.72 g, 9.47 mmol), 9,9'-spirobifluorene-2-boronic acid (**5**) (4.06 g, 11.28 mmol), Cs₂CO₃ (7.51 g, 23.02 mmol), and dioxane (30 ml) were added into the above round bottomed flask, respectively. The mixture was recharged with N₂ and refluxed at 85 °C for 12 h. The solution was cooled, quenched by water (20 ml) and extracted with ethylacetate (30 ml). The organic layer was washed with water (30 ml) and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography over

silica gel using dichloromethane/light petroleum (1:2, v/v) as an eluent to obtain a white solid (**6**) (1.32 g, 30.2%).

¹H NMR (400 MHz, CDCl₃)–δ(ppm): 6.734–6.778 (m, 3H), 7.097–7.168 (m, 3H), 7.367–7.417 (m, 4H), 7.644–7.665 (d, 1H), 7.817–7.843 (d, 1H), 7.868–7.915 (m, 3H), 7.975–7.995 (d, 1H), 8.131–8.155 (d, 1H), 8.815 (s, 1H).

2.2.2. Tetrakis[2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridinato-C³, N](μ-dichloro)diiridium ((sfp-5CF₃-py)₂Cl)₂ (**7**) and bis[2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridinato-C³, N] iridium(acetyl acetonate) [(sfp-5CF₃-py)₂Ir(acac)] (**8**) [14,21].

A mixture of IrCl₃·nH₂O (0.224 g, 0.62 mmol) and 2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridine (**6**) (0.646 g, 1.4 mmol) in 2-methoxyethanol (18 ml) and water (6 ml) was refluxed at 120 °C for 24 h under N₂ flow. Precipitate was filtered and washed with methanol, and water, respectively. An orange-red solid (**7**) was obtained.

[Ir(sfp-5CF₃-py)₂Cl]₂ (**7**) (0.23 g, 0.1 mmol), acetylacetone (0.025 g, 0.25 mmol) and sodium carbonate (0.041 g, 0.385 mmol) were mixed in 5 ml of 2-methoxyethanol. The reaction mixture was refluxed for 16 h under nitrogen and cooled before water was added. Precipitate was filtered off and washed by water, and methanol, respectively. The crude was purified by column chromatography over silica gel using an eluent of dichloromethane/light petroleum (1:3, v/v) to afford an orange-red solid (**8**) (0.08 g, 33%).

¹H NMR (400 MHz, CDCl₃)–δ(ppm): 1.55 (s, 3H, CH₃), 1.84 (s, 3H, CH₃), 5.29 (s, 1H, CH), 6.59–6.61 (d, 2H, Pyridine), 6.65–6.67 (t, 2H, Pyridine), 6.94–7.04 (m, 7H, Fluorene), 7.06–7.13 (m, 5H, Fluorene), 7.16–7.20 (t, 1H, Fluorene), 7.30–7.38 (m, 6H, Fluorene), 7.69–7.76 (m, 2H, Fluorene), 7.82–7.89 (m, 7H, Fluorene), 8.81 (s, 1H, Pyridine), 9.63 (s, 1H, Pyridine). MS (*m/z*): 1212.25 [M]⁺ (calcd for C₆₇H₄₁F₆IrN₂O₂, 1212.27). Elemental analysis: calcd. for C₆₇H₄₁F₆IrN₂O₂: C, 66.38; H, 3.41; N, 2.31, found C, 66.02; H, 3.37; N, 2.22.

2.2.3. Bis[2-(9,9'-spirobifluorene-2-yl)-5-trifluoromethylpyridinato-C³, N] iridium (2-picolinic acid) [(sfp-5CF₃-py)₂Ir(pic)] (**9**) [14,22]

To a mixture of [Ir(sfp-5CF₃-py)₂Cl]₂ (**7**) (0.345 g, 0.15 mmol) and Na₂CO₃ (0.049 g, 0.465 mmol) in 2-methoxyethanol (7 ml), picolinic acid (0.051 g, 0.413 mmol) was added. The reaction mixture was kept at 120 °C for 20 h under N₂ flow and cooled to room temperature. Water (10 ml) was added and precipitate was filtered off. Crude product was washed by water, and methanol, respectively, and then purified by column chromatography over silica gel using ethylacetate/light petroleum (1:3, v/v) as an eluent to collect an orange-yellow solid (**9**) (0.34 g, 90.8%).

¹H NMR (400 MHz, CDCl₃)–δ(ppm): 6.61–6.63 (d, 2H, Pyridine), 6.66–6.79 (m, 4H, Pyridine), 6.82–6.84 (d, 2H, Pyridine), 7.01–7.23 (m, 11H, Fluorene), 7.30–7.44 (m, 7H, Fluorene), 7.74–7.91 (m, 9H, Fluorene), 7.97–7.98 (t, 1H, Fluorene), 8.37–8.39 (d, 1H, Pyridine), 9.12 (s, 1H, Pyridine). MS (*m/z*): 1235.28 [M]⁺ (calcd for C₆₈H₃₈F₆IrN₃O₂, 1235.25). Elemental analysis: calcd. for C₆₈H₃₈F₆IrN₃O₂: C, 66.12; H, 3.10; N, 3.40, found C, 65.76; H, 3.06; N, 3.31.

2.3. Device fabrication and testing

Poly(3,4-ethylene dioxythiophene): poly(styrenesulfonic acid) (PEDOT: PSS), poly(vinylcarbazole) (PVK), 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD), 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBi), 4,4-bis(9H-carbazol-9-yl)biphenyl (CBP), 1,3-bis(9H-carbazol-9-yl) benzene (mCP), bis(4,6-difluorophenylpyridine)-picolinate iridium(III) (FIrPic), LiF and Al were purchased from Acros Organics. Indium tin oxide (ITO) glass substrate with a

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