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Tuning iridium(III) complexes containing 2-benzo[*b*]thiophen-2-yl-pyridine based ligands in the red region

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Abstract

Synthesis and characterization of four iridium(III) complexes containing 2-benzo[*b*]thiophen-2-yl-pyridine based ligands are reported. The absorption, emission, electrochemistry, and thermostability of the complexes were systematically investigated. The (btmp)$_2$Ir(acac) (btmp = 2-benzo[*b*]thiophen-2-yl-4-methyl-pyridyl, acac = acetyl acetone) was characterized using X-ray crystallography. Calculation on the electronic ground state for (btmp)$_2$Ir(acac) was carried out using B3LYP density functional theory, HOMO levels are a mixture of Ir and btmp ligand orbitals, while the LUMO is predominantly btmp ligand based. Introduction of substituents (CH_3, CF_3) into pyridyl ring in a typical red emitter (btp)$_2$Ir(acac) leads to a marked decrease in the sublimation temperature, which is more suitable for OLEDs process. Electrochemical studies showed that (btmp)$_2$Ir(acac) has a slightly lower oxidation potential, but (btfmp)$_2$Ir(acac), (btfmp)$_2$Ir(dbm), and (btfmp)$_2$Ir(pic) (btfmp = 2-benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridine, dbm = dibenzoylmethane, pic = 2-picolinic acid) containing CF_3 group are much difficult to oxidate than (btp)$_2$Ir(acac). The emission characteristics of these complexes can be tuned by either changing the substituents and their position on 2-benzo[*b*]thiophen-2-yl-pyridine or using different monoanionic ligands, showing emission λ_{max} values from 604 to 638 nm in CH_2Cl_2 solution at room temperature.

Keywords: Cyclometalated iridium complex; Red phosphorescent emitting material; Single crystal structure

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1. Introduction

Phosphorescent materials have attracted extensive attention in recent years owing to their potential advantages of harvesting excitons from both singlet and triplet states in the OLEDs [1–6]. Cyclometalated iridium(III) complexes received the most wide study partly due to tuning color emission from red to blue by using different ligands [7–9]. Many of green phosphorescent materials were obtained and successfully used in organic electrophosphorescent devices [10–13]. Forrest and co-workers reported a red phosphorescent dye (btp)$_2$Ir(acac), bis(2-benzo[*b*]thiophen-2-yl-pyridinato-N,C$^{3'}$)iridium(III) acetylacetonate, which was employed as a dopant in devices with $\eta_{ex} = 7\%$ [14]. But for the red phosphorescent dye, since the luminescence quantum yields tend to decrease with an increase in the emission peak wavelength according to the energy gap law [15], it is difficult to find a good performance material for OLEDs, there are only a limited number of high emissive phosphors suitable to red devices. In this study, we designed and synthesized four new red phosphorescent iridium complexes based on (btp)$_2$Ir(acac) skeleton, the emission characteristics of these complexes can be tuned by either changing the substituents and their position on 2-benzo[*b*]thiophen-2-yl-pyridine or using different monoanionic ligands.

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2. Experimental

2-Chloro-5-trifluoromethyl-pyridine, 2-bromo-4-methyl-pyridine, benzo[*b*]thiophene-2-boronic acid, $IrCl_3 \cdot nH_2O$, $Pd(PPh_3)_4$, acetylacetone, dibenzoylmethane, and 2-picolinic acid were from Aldrich, and used without further purification. All procedures were carried out in inert gas atmosphere despite the air stability of the compounds. ^1H NMR spectra were recorded on Bruker Avance 300 MHz instrument. Elemental analyses were performed on VarioEL III CHNS instrument. Absorption spectra were measured on UV–Vis–NIR scanning spectrophotometer. Photoluminescence (PL) spectrum was measured with a F-4500 Fluorescence Spectrometer. Thermogravimetric analysis (TGA) was performed by a TGA 2950 thermal analyzer (TA Co.) under N_2 stream with a scanning rate of 10 °C/min.

2.1. Electrochemistry

Cyclic voltammetry experiments were performed with a MCP-1 electrochemical analyzer (JiangFen co., china). All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, a Pt wire auxiliary electrode, and Ag/AgCl reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential. The solvent was CH_2Cl_2 and the supporting electrolyte was 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate.

2.2. X-ray crystallography

Intensity data for $(btmp)_2Ir(acac)$ were collected at room temperature ($T = 296$ K) on a BRUKER SMART APEX II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for LP factors and absorption was applied by using the SADABS program. The structure was solved by direct methods and refined by full-matrix least-squares refinement on F^2 using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed at calculated positions and refined using riding model with C–H distances in the range 0.93–0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). A summary of crystal data and refinement parameters is given in Table 1.

Table 1
Crystal data and structure refinement for $(btmp)_2Ir(acac)$

Identification code	$(btmp)_2Ir(acac)$
Empirical formula	$C_{33}H_{27}IrN_2O_2S_2$
Formula weight	739.89
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system, space group	monoclinic, $P2(1)/n$
Unit cell dimensions	
a (Å)	11.2185(10)
b (Å)	16.6343(14)
c (Å)	16.0375(14)
α (°)	90
β (°)	100.813(2)
γ (°)	90
Volume (Å^3)	2939.7(4)
Z, D_{calc} (Mg/m^3)	4, 1.672
Absorption coefficient (mm^{-1})	4.717
$F(000)$	1456
Crystal size (mm)	$0.28 \times 0.16 \times 0.13$
θ Range for data collection (°)	1.78–25.00
Limiting indices	$-13 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 19$, $-12 \leqslant l \leqslant 19$
Reflections collected/unique [R_{int}]	14746/5167 [0.0248]
Completeness to $\theta = 25.00$ (%)	99.9
Absorption correction	multi-scan
Maximum and minimum transmission	0.5791 and 0.3518
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5167/0/365
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0219$, $wR_2 = 0.0484$
R indices (all data)	$R_1 = 0.0308$, $wR_2 = 0.0509$
Largest difference in peak and hole (e Å^{-3})	0.898 and −0.332

2.3. Synthesis and characterization of ligands

2-Benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridine (Hbtfmp) [16] and 2-benzo[*b*]thiophen-2-y- 4-methyl-pyridine (Hbtmp) were synthesized according to the literature procedure [17]. A detailed description is provided only for Hbtmp. 2-Bromo-4-methyl-pyridine (4.4 g, 0.0195 mol), benzo[*b*]-thiophene-2-boronic acid (3.47 g, 0.0195 mol), $Pd(PPh_3)_4$ (0.68 g), toluene (60 ml), ethanol (20 ml), and 2 M Na_2CO_3 (60 ml) were heated to reflux for 6 h. It was then cooled, water was added, extracted with toluene. The combined organic layer was washed with water, dried over $MgSO_4$, filtered, and the filtrate was evaporated under reduced pressure, the residue was chromatographed using *n*-hexane/dichloromethane (1:1) as eluent to afford the white powders in 73% yield.

Hbtmp: White powders. Yield: 73%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.42 (d, 1H), 7.78 (m, 3H), 7.52 (s, 1H), 7.27 (t, 2H), 6.92 (d, 1H), 2.31 (s, 3H). *Anal.* Calc.: C, 74.67; H, 4.889; N, 6.222. Found: C, 74.66; H, 4.822; N, 5.965%.

Hbtfmp: White powders, Yield: 75%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.80 (s, 1H), 7.80 (m, 5H), 7.3 (t, 2H). *Anal.* Calc.: C, 60.22; H, 2.867; N, 5.018. Found: C, 60.09; H, 2.693; N, 4.913%.

2.4. Synthesis and characterization of iridium complex

Iridium(III) complexes were obtained in two steps using standard procedure [18]. These iridium complexes were prepared by a similar procedure, only the synthesis of $(btmp)_2Ir(acac)$ is presented in detail. A mixture of 1.00 g (2.835 mmol) of $IrCl_3 \cdot nH_2O$, 1.27 g (5.670 mmol) of

Hbtmp, 80 ml of 2-ethoxyethanol, and 20 ml of water was refluxed at 120 °C for 24 h. After cooling down to room temperature, the chloride-bridged dimer was isolated by addition of water followed by filtration and methanol wash. The dimer was not further characterized and was used directly in subsequent reaction. A mixture of 1.70 g (1.270 mmol) of the dimer, 0.32 g (3.182 mmol) of acetylacetone, 1.2 g Na_2CO_3, and 100 ml of 2-ethoxyethanol was refluxed for 16 h. After cooling down to room temperature, the solvent was removed by vacuum, the crude product was washed with methanol to remove any unreacted acetylacetone. The red powder was afforded in 40% yield with sublimation in a vacuum of 100 Pa. The structures and abbreviations of Ir complexes used in this study are shown in Fig. 1.

$(btmp)_2Ir(acac)$: bis(2-benzo[*b*]thiophen-2-yl-4-methyl-pyridinato-N,$C^{3'}$)iridium(III) (acetylacetonate) (red powder, yield 45%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.20 (d, 2H), 7.55 (d, 2H), 7.37 (s, 2H), 6.97 (t, 2H), 6.77 (m, 4H), 6.20 (d, 2H), 5.17 (s, 1H),2.55 (s, 6H), 1.70 (s, 6H). *Anal.* Calc.: C, 52.93; H, 3.521; N, 3.588. Found: C, 52.67; H, 3.448; N, 3.539%.

$(btfmp)_2Ir(acac)$ [16]: bis(2-benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridinato-N,$C^{3'}$)iridium(III) (acetylacetonate) (red powder, yield 65%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.56 (s, 2H), 7.65 (d, 2H), 7.60 (t, 2H), 7.10 (m, 4H), 6.79 (t, 2H), 6.16 (d, 2H), 5.25 (s, 1H), 1.75 (s, 6H). *Anal.* Calc.: C, 46.85; H, 2.485; N, 3.313. Found: C, 46.56; H, 2.455; N, 3.277%.

$(btfmp)_2Ir(pic)$: bis(2-benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridinato-N,$C^{3'}$)iridium(III) picolinate (red powder, 40%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.79 (s, 1H), 8.44 (t, 2H), 8.17 (m, 4H), 7.96 (m, 2H), 7.71 (m, 2H), 7.46 (s, 1H), 7.26 (m, 2H), 6.98 (m, 2H), 6.15 (d, 1H), 5.91 (d, 1H). *Anal.* Calc.: C, 48.33; H, 2.488; N, 4.284. Found: C, 47.91; H, 2.316; N, 4.305%.

$(btfmp)_2Ir(dbm)$: bis(2-benzo[*b*]thiophen-2-yl-5-trifluoromethyl-pyridinato-N,$C^{3'}$)iridium(III) (dibenzoylmethane) (red powder, yield 58%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.64 (s, 2H), 7.86 (d, 2H), 7.64 (d, 8H), 7.35 (d, 2H), 7.23 (m, 4H), 7.13 (t, 2H), 6.85 (t, 2H), 6.55 (s, 1H), 6.25 (d, 2H). *Anal.* Calc.: C, 53.13; H, 2.574; N, 2.883. Found: C, 52.85; H, 2.529; N, 2.831%.

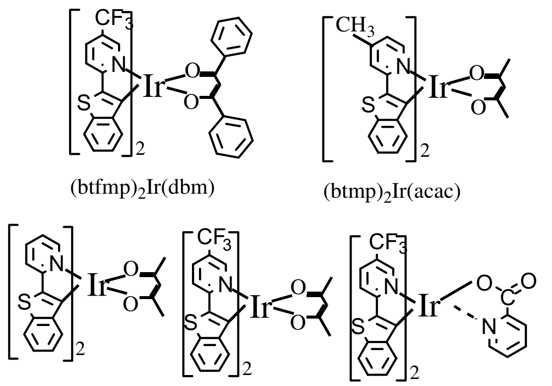
3. Results and discussion

3.1. Crystal structure of $(btmp)_2Ir(acac)$

Single crystals of $(btmp)_2Ir(acac)$ were grown from sublimation and characterized using crystallography. The ORTEP drawing of the complex is shown in Fig. 2. Selected parameters of the molecular structure are listed in Table 2. The complex has a distorted octahedral coordination geometry around iridium atom and the two nitrogen atoms of btmp ligands exhibit *cis*-C–C and *trans*-N–N chelate dispositions. The Ir–C bonds ($Ir–C_{av} = 2.003(3)$ Å) are shorter than the Ir–N bonds ($Ir–N_{av} = 2.046(3)$ Å). The Ir–C bonds of $(btmp)_2Ir(acac)$ are equal to that of $(ppy)_2Ir(acac)$ (Ir–C, 2.003(9) Å), while the Ir–N bonds are longer than the value of the latter (Ir–N, 2.010(9) Å), but the Ir–O bonds ($Ir–O_{av} = 2.126$ Å) are 0.020 Å shorter than the value of $(ppy)_2Ir(acac)$ [7]. The N(1)–Ir(1)–N(2) (177.59(11)°), C(1)–Ir(1)–N(1) (80.00(12)°), C(18)–Ir(1)–N(2) (80.13(13)°), N(1)–Ir(1)–O(1) (94.77(10)°), C(18)–Ir(1)–O(1) (89.61(11)°), and O(1)–Ir(1)–O(2) (89.13(10)°) bond angles are typical for cyclometalates and β-diketonate derivatives of Ir [7,19,20]. All other features appear to be normal.

3.2. DFT calculations

DFT calculation on the electronic ground state of $(btmp)_2Ir(acac)$ was carried out at the B3LYP/LANL2DZ level [21,22]. A similar approach has been used to investigate the properties of $Ir(ppy)_3$ and $(ppy)_2Ir(acac)$ [23]. The HOMO and LUMO energies were determined using minimized singlet geometries to approximate the ground state. The results of the optimized structure for $(btmp)_2Ir(acac)$ are summarized in Table 2, which are compared with X-ray diffraction studies. The calculated $Ir–C_{av}$ bond length



$(btfmp)_2Ir(dbm)$ $(btmp)_2Ir(acac)$

$(btp)_2Ir(acac)$ $(btfmp)_2Ir(acac)$ $(btfmp)_2Ir(pic)$

Fig. 1. Iridium complexes and their abbreviations in this study.

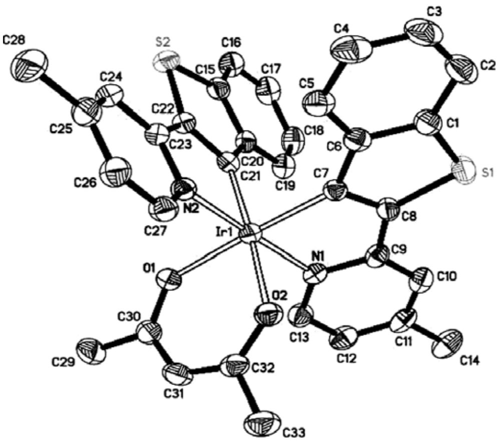


Fig. 2. ORTEP diagram of $(btmp)_2Ir(acac)$.

Table 2
Comparison of calculated bond lengths for $(btmp)_2Ir(acac)$ with experimental values from X-ray diffraction

	Calculated	Experimental
Bond lengths (Å)		
Ir(1)–C(7)	2.0181	2.006(3)
Ir(1)–C(21)	2.0181	1.999(3)
Ir(1)–N(1)	2.0675	2.046(3)
Ir(1)–N(2)	2.0675	2.047(3)
Ir(1)–O(1)	2.1697	2.124(2)
Ir(1)–O(2)	2.1697	2.129(2)
S(1)–C(1)	1.8172	1.731(4)
S(1)–C(8)	1.8259	1.745(3)
S(2)–C(15)	1.8172	1.743(4)
S(2)–C(22)	1.8259	1.746(4)
Bond angles (°)		
N(1)–Ir(1)–N(2)	178.20	177.59(11)
N(1)–Ir(1)–C(1)	80.36	80.00(12)
N(2)–Ir(1)–C(18)	80.36	80.13(13)
N(1)–Ir(1)–O(1)	92.93	94.77(10)
C(18)–Ir(1)–O(1)	90.14	89.61(11)
O(1)–Ir(1)–O(2)	86.22	89.13(10)

of 2.0181 Å is 0.0151 Å longer than the experimental value. The $Ir–N_{av}$ bond length of 2.0675 Å and $Ir–O_{av}$ bond length of 2.1697 Å are 0.0215 and 0.0437 Å longer than the measured values, respectively. The calculated values for C–Ir–N, N–Ir–N, N–Ir–O, O–Ir–O chelate angles are consistent with the corresponding experimental values determined in the X-ray structure of $(btmp)_2Ir(acac)$. The HOMO and LUMO levels are shown in Fig. 3. The HOMO (−4.806 eV) consists of a mixture of 2-benzo[*b*]thiophen-2-yl ring of btmp ligands (51.5%) and Ir orbitals (31.2%), while the LUMO (−1.631 eV) is mostly on the 2-benzo[*b*]thiophen-2-yl ring (32.1%) and pyridyl ring (57.0%) of btmp ligands. The composition (%) of HOMO and LUMO for $(btmp)_2Ir(acac)$ is shown in Table 3.

Table 3
Composition (%) of HOMO and LUMO for $(btmp)_2Ir(acac)$

MOs	Ir	Benzo[*b*]thiophene ring	Pyridyl ring	Methyl on pyridine	acac
HOMO	31.2	51.5	14.4	0.08	3.4
LUMO	6.1	32.1	57.0	2.3	2.4

3.3. Thermal stability

In the materials sublimation process, the pure emitting materials were obtained under 300–500 °C in ordinary train sublimation equipment. Lower sublimation temperature is beneficial to materials purity and devices fabrication. The vaporization temperature was determined by a TGA thermal analyzer under N_2 stream with a scanning rate of 10 °C/min. The 10% weight loss temperatures ($\Delta T_{10\%}$) of these iridium complexes are in the range of 338–348 °C, while the value of an ordinary red dye $(btp)_2Ir(acac)$ is 368 °C, indicating introduction of substituents (CH_3, CF_3) into pyridyl ring in $(btp)_2Ir(acac)$ leading to a marked decrease in the vaporization temperature, which is more suitable to materials purity and devices fabrication [24,25].

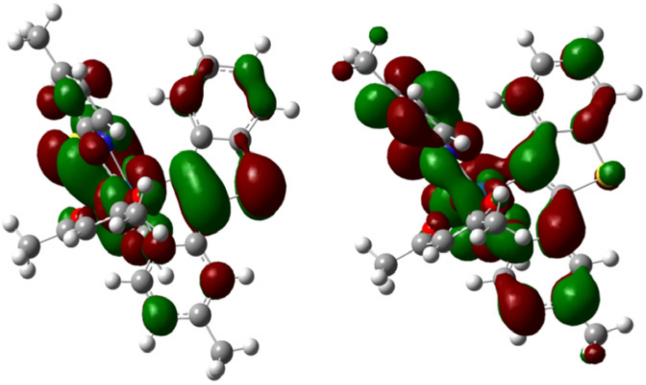


Fig. 3. Density functional theory calculation (DFT) of HOMO (left) and LUMO (right) for $(btmp)_2Ir(acac)$.

3.4. Cyclic voltammetric studies

The electrochemical properties of these complexes were characterized using cyclic voltammetry, the redox data are given in Table 4. All studied complexes showed reversible oxidation waves in the range of 680–1073 mV versus Ag/AgCl, which can be attributed to the oxidation of the iridium(III). No reduction waves were measured in the complexes up to −3.0 V. The oxidation wave value of $(btmp)_2Ir(acac)$ with a electron-donating group (CH_3) on the 4-positon of pyridyl ring is 680 mV, which is lower than that of $(btp)_2Ir(acac)$ (720 mV, in this measurement condition), while the $(btfmp)_2Ir(acac)$, $(btfmp)_2Ir(dbm)$, and $(btfmp)_2Ir(pic)$ containing electron-withdrawing groups (CF_3) on 5-positon of pyridyl ring have higher values (941–1073 mV) relative to that of $(btp)_2Ir(acac)$. So, incorporating electron-donating group on the 4-positon of pyridyl ring of ligand gives a decrease in the oxidation potential, while introduction of electron-withdrawing groups into the 5-positon of pyridyl ring of ligand leads to a marked increase in value. Meanwhile, different ancillary ligands also lead to changing oxidation potentials of iridium complexes, the ligand of 2-picolinic acid containing 'deficient electron' atom N makes the iridium(III) more difficult to oxidate than that of β-diketonates. This is consistent with our DFT calculation, the HOMO orbitals of $(btmp)_2Ir(acac)$ are a mixture of Ir and btmp, incorporation of substituents on cyclometalated ligands was shown to affect the oxidation potential of the iridium ion.

3.5. Photophysical properties

Absorption and room-temperature emission spectra were recorded for all of the complexes as shown in Figs. 4 and 5, respectively. The data are summarized in Table 4. The

Table 4
Absorption, emission, ϕ_{pl}, TGA, and redox properties of Ir(III) complexes

Complexes	Abs, λ[a] (nm) (log ε)	λ_{em}[b] (nm)	ϕ_{pl}[c]	Redox (mV)[d], $E_{1/2}^{ox}$	TGA (°C)[e]
$(btmp)_2Ir(acac)$	280 (4.60), 322 (4.46), 334 (4.45), 449 (3.84), 477 (3.94)	604	0.025	680	338
$(btfmp)_2Ir(acac)$	290 (4.57), 335 (4.49), 352 (4.45), 369 (4.36), 482 (3.90), 513 (4.00)	638	0.040	947	341
$(btfmp)_2Ir(pic)$	294 (4.54), 345 (4.44), 368 (4.31), 498 (4.01)	627	0.048	1073	340
$(btfmp)_2Ir(dbm)$	292 (4.68), 334 (4.52), 354 (4.49), 371 (4.44), 479 (3.83), 512 (3.92)	637	0.125	941	348
$(btp)_2Ir(acac)$	283 (4.62), 326 (4.45), 355 (4.35), 482 (3.92)	613	0.017	720	368

[a] Measured in CH_2Cl_2 solution at a concentration of 10^{-5} mol/L.

[b] Measured in CH_2Cl_2 solution at 298 K.

[c] Measured in toluene at 298 K. Excitation wavelength was 400 nm for all complexes, $Ir(ppy)_3$ ($\phi_{pl} = 0.4$ in toluene) was used as the reference for quantum yield (ϕ_{pl}).

[d] Measured in CH_2Cl_2 at a concentration of 10^{-3} M and scan rate was 80 mV s^{-1}, values are reported relative to Ag/AgCl.

[e] Temperature listed is at a point of 10% weight loss.

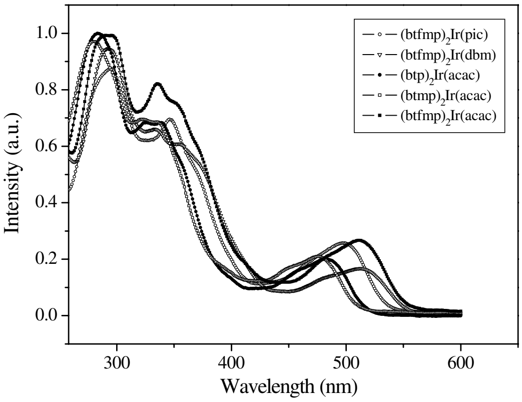


Fig. 4. Absorption spectra for $(btp)_2Ir(acac)$, $(btmp)_2Ir(acac)$, $(btfmp)_2Ir(acac)$, $(btfmp)_2Ir(pic)$, and $(btfmp)_2Ir(dbm)$ complexes in CH_2Cl_2 solution.

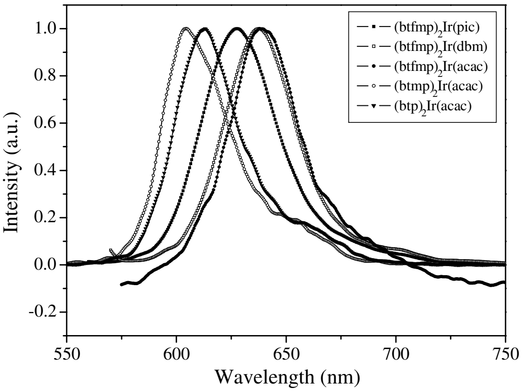


Fig. 5. Emission spectra for $(btp)_2Ir(acac)$, $(btmp)_2Ir(acac)$, $(btfmp)_2Ir(acac)$, $(btfmp)_2Ir(pic)$, and $(btfmp)_2Ir(dbm)$ complexes in CH_2Cl_2 solution at room temperature.

intense absorption bands at higher energy were assigned to π–π* ligand-centered (LC) transitions, and low energy bands in the range of 420–560 nm to singlet and triplet MLCT transitions. The ^{1}MLCT and ^{3}MLCT were not well resolved, which has been observed from the complex $(btp)_2Ir(acac)$ [7,18]. A large Stokes shift between the ^{3}MLCT absorption and emission bands was observed, so these complexes should emit from an excited state that is predominantly due to $^3(\pi–\pi^*)$ [18,20].

Strong spin–orbit coupling in the iridium complexes leads to efficient phosphorescence, these complexes exhibit high solution phosphorescence quantum yields ($\phi_{pl} = 0.025–0.125$) at room temperature under air free condition. These values are high comparative to typical red phosphorescent materials $(btp)_2Ir(acac)$ ($\phi_{pl} = 0.017$) under the same measurement condition used $Ir(ppy)_3$ as the reference for quantum yield.

Incorporation of a weak electron-donating group (CH_3) on the 4-position of the pyridyl of 2-benzo[*b*]thiophen-2-yl-pyridine in $(btp)_2Ir(acac)$ raises the LUMO level, enlarges the gap between HOMO and LUMO levels, and hence a 9-nm blue shift in the $(btmp)_2Ir(acac)$ is observed in comparison to that of $(btp)_2Ir(acac)$ (613 nm) in CH_2Cl_2 solution [18]. Substitution of a electron-withdrawing group (CF_3) on the 5-position of pyridyl ring results in lowering LUMO level, so large red shifts were observed. Meanwhile the different monoanionic ligands also affect the emission wavelength of these complexes, the $(btfmp)_2Ir(pic)$ with the monoanionic ligand of 2-picolinic acid shows the maximum emission wavelength of 627, 10 nm blue shift in comparison to that of $(btfmp)_2Ir(acac)$ (638 nm) and $(btfmp)_2Ir(dbm)$ (637 nm) in CH_2Cl_2 solution. The emission characteristics of these complexes can be tuned by either changing the substituents and their position on 2-benzo[*b*]thiophen-2-yl-pyridine or using different monoanionic ligands. The photophysical properties for these iridium complexes are consistent with the result of our DFT calculation.

4. Conclusion

In summary, we report four Iridium complexes containing 2-benzo[*b*]thiophen-2-yl-pyridine based ligands with the maximum emission wavelength in the range of 604–638 nm in CH_2Cl_2 solution. The emission characteristics of these complexes can be tuned by either changing the substituents and their position on 2-benzo[*b*]thiophen-2-yl-pyridine or using different monoanionic ligands. These iridium complexes with excellent sublimation property are easily prepared, making them good candidates for the fabrication of devices.

5. Supplementary material

CCDC 280190 contains the supplementary crystallographic data for $(btmp)_2Ir(acaac)$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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