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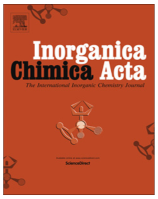

Color tuning of cyclometalated 2-phenylbenzo[d]oxazole-based iridium (III) complexes through modification of different N^O ancillary ligands

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ABSTRACT

Four new cyclometalated bo-based iridium(III) complexes with different N^O ancillary ligands, $[Ir(bo)_2pic]$ (**1**), $[Ir(bo)_2prz]$ (**2**), $[Ir(bo)_2bop]$ (**3**) and $[Ir(bo)_2btp]$ (**4**) (bo = 2-phenylbenzo[d]oxazole, pic = picolinate, prz = pyrazinate, bop = 2-benzoxazol-2-yl phenol, btp = 2-benzothiazol-2-yl phenol), have been synthesized and investigated by optical spectroscopy, electrochemistry as well as density functional theory (DFT). The crystal structures of **1**, **2** and **4** have been determined, which show that each adopts the distorted octahedral coordination geometry. They exhibit intense green to orange phosphorescence (λ_{max} = 531–598 nm) with quantum yields of 0.19–0.94 and lifetimes of 0.078–0.468 μs in solution at 298 K. The broad range color tuning of complexes **1**–**4** is dependent on the ancillary ligand structure. The cyclic voltammetry has been measured, showing a quasireversible, metal-centered oxidation with potentials at 1.00–1.49 V. The frontier molecular orbital diagrams and the lowest-energy electronic transitions of **1**–**4** have been calculated with density functional theory (DFT) and time-dependent DFT (TD-DFT).

1. Introduction

In recent years, a considerable amount of interests have been drawn to the application of iridium(III) complexes in organic light-emitting devices (OLEDs), because of their saturated phosphorescence color, high phosphorescence efficiency, and physical compatibility [1–4]. Particularly, well-defined molecular design methods for efficient phosphorescence color tuning are currently under active investigation with the aim of achieving full-color displays [5]. Previous researches found that the emission color of the heteroleptic iridium complexes $[Ir(C^\wedge N)_2(LX)]$ are largely governed by the nature of the cyclometalated ligands (C^N), while the ancillary ligand (LX) operated insignificant control [6–8]. But such a standpoint has been changed. Using appropriate ancillary ligands can also achieve the tuning of emission colors for Ir(III) based complexes [9]. For example, the emissions of $Ir(dfppy)_2(LX)$ [10] can be tuned from blue to red by changing ancillary ligands. Afterward, a series of $Ir(dfpypy)_2(N^\wedge O)$ and $Ir[(RO)_2pypy]_2(N^\wedge O)$ heteroleptic iridium(III) complexes were reported, exhibiting intense blue to yellow phosphorescence by changing N^O ligands [11]. More recently, we explored the influence of three different hetero-atom (S, O and N) ancillary ligands on the photophysical and electrochemical properties of $[Ir(btp)_2(LX)]$ iridium(III) complexes [12]. These research support that the ability to tune the emission color by varying the structure of ancillary ligands.

Iridium(III) complex with bis(2-phenylbenzo[d]oxazole) as the ligand, $Ir(bo)_2(acac)$, was first reported by Thompson et al. [13]. Subsequently, Chen et al. [14] studied $Ir(bo)_2(acac)$ derivatives with substituents in phenyl ring and showed that the emissive colors of the materials can be finely tuned by systematic control of the nature and position of the substituents on the ligands. Very recently, we also reported $Ir(bo)_2(acac)$ derivatives with substituents on the benzoxazole ring and obtained a high phosphorescent iridium(III) complex with quantum yields of 53.5% [15].

The above results hence inspired us to further investigate the color tuning of bo-based iridium(III) complexes by choosing different ancillary ligands. Here, we design four heteroleptic iridium(III) complexes (**1**–**4**) with bo ligand as the parent compound and pic/prz/bop/btp ancillary ligands as tunable phosphors (Scheme 1). And, their photophysical and electrochemical properties are

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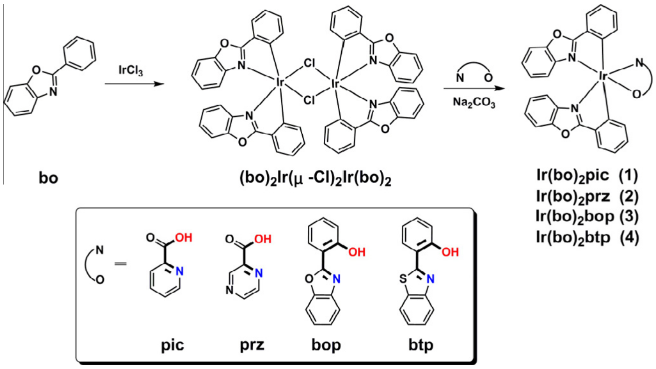

Scheme 1. Synthetic routes of Ir(III) complexes **1**–**4**.

discussed in detail. The absorption spectra are rationalized on the basis of density functional theory (DFT) and time-dependent DFT (TDDFT).

2. Experimental

2.1. Physical measurements

^{1}H NMR spectra were recorded on a Bruker AM 400 MHz instrument. Chemical shifts were reported in ppm relative to Me_4Si as internal standard. MALDI-TOF-MS spectra were recorded on a Bruker Autoflex ^{II}TM TOF/TOF instrument. The elemental analyses were performed on a Vario EL Cube Analyzer system. UV–vis spectra were recorded on a Hitachi U3900/3900H spectrophotometer. Fluorescence spectra were carried out on a Hitachi F-7000 spectrophotometer. Luminescence lifetime curves were measured on an Edinburgh Instruments FLS920P fluorescence spectrometer and the data were treated as one-order exponential fitting using OriginPro 8 software.

The luminescence quantum efficiencies were calculated by comparison of the fluorescence intensities (integrated areas) of a standard sample $Ir(ppy)_3$ and the unknown sample according to the equation [16,17].

$$\Phi_{\mathrm{unk}} = \Phi_{\mathrm{std}}\left(\frac{I_{\mathrm{unk}}}{I_{\mathrm{std}}}\right)\left(\frac{A_{\mathrm{std}}}{A_{\mathrm{unk}}}\right)\left(\frac{\eta_{\mathrm{unk}}}{\eta_{\mathrm{std}}}\right)^2$$

where Φ_{unk} and Φ_{std} are the luminescence quantum yield values of the unknown sample and $Ir(ppy)_3$ solutions ($\Phi_{\mathrm{std}} = 1.0$) [11], respectively. I_{unk} and I_{std} are the integrated fluorescence intensities of the unknown sample and $Ir(ppy)_3$ solutions, respectively. A_{unk} and A_{std} are the absorbance values of the unknown sample and $Ir(ppy)_3$ solutions at their excitation wavelengths, respectively. The η_{unk} and η_{std} terms represent the refractive indices of the corresponding solvents (pure solvents were assumed).

2.2. Synthesis of ligand

Picolinate (pic) and pyrazinate (prz) were purchased from Energy Chemical. 2-phenylbenzo[d]oxazole (bo) [18], 2-benzoxazol-2-yl phenol (bop) [19], 2-benzothiazol-2-yl phenol (btp) [20] were synthesized according to modification of literature procedures.

2.3. Synthesis of iridium complexes

The dichlorobridged iridium dimer $(bo)_2Ir(\mu\text{-}Cl)_2Ir(bo)_2$ was the critical precursor to synthesize complexes **1**–**4** and prepared according to the literature method [21]. A mixture of $IrCl_3{\cdot}3H_2O$ (1.0 equiv) and bo (2.2 equiv) in a mixture of 2-ethoxyethanol/H_2O (2:1, v/v) was refluxed for 12 h under nitrogen atmosphere. After cooling, the yellow solid precipitate was collected, washed with H_2O, EtOH and *n*-hexane. The cyclometalated Ir(III) chloro-bridged dimer was used directly in next step without further purification.

2.3.1. Synthesis of [Ir(bo)$_2$pic] (**1**)

A solution of ancillary ligand pic (0.5 mmol) and dichloro-bridged iridium dimer $(bo)_2IrCl_2Ir(bo)_2$ (0.2 mmol), and Na_2CO_3 (1.0 mmol) in 2-ethoxyethanol was refluxed for 24 h. After the mixture was cooled to room temperature, the solvent was evaporated. The residue was purified by column chromatography to give the pure product **1**. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0 Hz, 1H), 7.95–7.99 (m, 2H), 7.82 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.72 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 7.6 Hz, 1H), 7.35–7.41 (m, 2H), 7.27–7.29 (m, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.84–6.91 (m, 2H), 6.50–6.52 (m, 1H), 6.43 (d, J = 7.6 Hz, 1H). MS (MALDI-TOF) (m/z): 702.935 $[M+H]^+$. *Anal.* Calc. for $C_{32}H_{20}IrN_3O_4$ (%): C, 54.69; H, 2.87; N, 5.98. Found: C, 54.71; H, 2.86; N, 5.97%.

2.3.2. Synthesis of [Ir(bo)$_2$prz] (**2**)

Complex **2** was obtained by the method similar to the preparation of **1** using prz instead of pic ligand. Yield: 37%. ^{1}H NMR δ 9.43 (s, 1H), 8.73 (d, J = 2.8 Hz, 1H), 8.02 (s, 1H), 7.93–7.95 (m, 1H), 7.64–7.70 (m, 4H), 7.35–7.47 (m, 3H), 7.08 (t, J = 8.0 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.83–6.91 (m, 2H), 6.68 (d, J = 7.6 Hz, 1H), 6.44 (d, J = 7.6 Hz, 1H), 5.73 (d, J = 8.0 Hz, 1H). MS (MALDI-TOF) (m/z): 703.907 $[M+H]^+$. *Anal.* Calc. for $C_{31}H_{19}IrN_4O_4$ (%): C, 52.91; H, 2.72; N, 7.96. Found: C, 52.91; H, 2.70; N, 7.97%.

2.3.3. Synthesis of [Ir(bo)$_2$bop] (**3**)

Complex **3** was obtained by the method similar to the preparation of **1** using bop instead of pic ligand. Yield: 49%. ^{1}H NMR δ 7.93 (dd, J_1 = 2.0 Hz, J_2 = 8.0 Hz, 1H), 7.68∼7.75 (m, 3H), 7.60 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.28–7.38 (m, 2H), 7.13–7.24 (m, 3H), 6.95–7.03 (m, 3H), 6.79–6.88 (m, 4H), 6.70 (d, J = 7.6 Hz, 1H), 6.41–6.51 (m, 2H), 6.36 (d, J = 8.0 Hz, 1H), 6.11 (d, J = 8.4 Hz, 1H). MS (MALDI-TOF) (m/z): 791.055 $[M+H]^+$. *Anal.* Calc. for $C_{39}H_{24}IrN_3O_4$ (%): C, 59.23; H, 3.06; N, 5.31. Found: C, 59.22; H, 3.07; N, 5.30%.

2.3.4. Synthesis of [Ir(bo)$_2$btp] (**4**)

Complex **4** was obtained by the method similar to the preparation of **1** using btp instead of pic ligand. Yield: 51%. ^{1}H NMR δ 7.78–7.81 (m, 2H), 7.71 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.27–7.35 (m, 3H), 7.02–7.23 (m, 5H), 6.81–7.99 (m, 4H), 6.63–6.73 (m, 3H), 6.47 (d, J = 8.4 Hz, 1H), 6.35 (d, J = 7.6 Hz, 1H), 6.27 (t, J = 7.6 Hz, 1H). MS (MALDI-TOF) (m/z): 806.970 $[M+H]^+$. *Anal.* Calc. for $C_{39}H_{24}IrN_3O_3S$ (%): C, 58.05; H, 3.00; N, 5.21. Found: C, 58.06; H, 3.02; N, 5.19%.

2.4. Crystal structure determination

X-ray diffraction data were collected with an Agilent Technologies Gemini A Ultra diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Data collection and reduction were processed with CrysAlisPro software [22]. The structure was solved and refined using Full-matrix least-squares based on F^2 with program SHELXS-97 and SHELXL-97 [23] within Olex2 [24]. All non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated positions and refined as riding atoms with a uniform value of *U*iso.