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Syntheses, structures and properties of cyclometalated iridium(III) complexes based on 2-phenyl-5-nitropyridyl and different strong-field ancillary ligands

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ABSTRACT

The reactions of [Ir(5-NO_2-ppy)$_2$(PPh_3)Cl] (5-NO_2-ppy = 2-phenyl-5-nitropyridyl, PPh_3 = triphenylphosphine, **1**) with pseudohalides, replacing the weak π donor Cl^- with strong σ donors and π acceptors, lead to three new iridium(III) cyclometalated complexes [Ir(5-NO_2-ppy)$_2$(PPh_3)(L)] (L = NCO^-, **2**; NCS^-, **3**; N_3^-, **4**) based on 2-phenylpyridyl (ppy) derivative, PPh_3 and different pseudohalogen strong-field ancillary ligands. **2**–**4** are unambiguously characterized and their crystal structures are also determined by X-ray crystallography. The HOMO–LUMO electronic energy gaps of **1**–**4** estimated from the cyclic voltammetry measurements are comparable with those calculated from the UV–Vis absorption spectra, which are both in the order of **3** > **1** > **2** > **4**. Furthermore, the electrochemical and photophysical properties of **1**–**4** show that the introduction of the electron-withdrawing nitro group to the pyridyl ring of the ppy backbone narrows the HOMO–LUMO electronic energy gaps, compared with those of corresponding ppy-containing iridium(III) complexes.

1. Introduction

In recent years, iridium complexes have stimulated continuing interest in a wide range of chemical areas [1–3]. The extensive applications of iridium complexes in fields of organic light emitting devices (OLEDs) [4,5], catalysts [6,7], oxygen sensors [8,9] and bio-analytical reagents [10,11] show capacious research foreground. Cyclometalated iridium(III) complexes have especially received considerable attention because of their outstanding photochemical and photophysical properties, which make this class of complexes be widely applied to a variety of photonic applications and emissive materials in OLEDs [12–15].

Cyclometalated iridium(III) complexes containing 2-phenylpyridyl (ppy) have been investigated sufficiently and widespreadly in the field of OLEDs, because these complexes are known to exhibit high triplet quantum yields due to mixing the singlet and the triplet excited states via spin–orbit coupling, which enhances the triplet state subsequently, leading to high phosphorescence efficiencies [16,17]. Furthermore, in order to achieve tuning the emission wavelengths of ppy-containing cyclometalated iridium(III) complexes over the entire visible region, it is necessary to adjust the electronic energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the complexes. The introduction of electron-donating [18,19] or withdrawing groups [20–21] to ppy frameworks can modify the HOMO–LUMO energy gaps efficiently. However, the effect of substituents, such as simple functional electron-donating or withdrawing groups, and the dependence on their positions on the phenyl or pyridyl ring in the ppy backbone, are still worthy of being studied.

The dichloro-bridged iridium dimer [Ir(5-NO_2-ppy)$_2$Cl]$_2$ (5-NO_2-ppy = 2-phenyl-5-nitropyridyl), in which the strongly electron-withdrawing nitro group is introduced to the pyridyl ring of the ppy ligand, has been firstly reported by Watts et al. [22]. Thompson et al. has also reported the 5-NO_2-ppy-containing luminescent cyclometalated platinum(II) complex [(5-NO_2-ppy)Pt(acac)] (acac = acetylacetonate), which contains only one 5-NO_2-ppy ligand and shows a four-coordinated square planar geometry [23]. A phosphorescent cyclometalated iridium(III) complex [Ir(5-NO_2-ppy)$_2$(PPh_3)Cl] (PPh_3 = triphenylphosphine, **1**) containing 5-NO_2-ppy with six-coordinated distorted-octahedral conformation was reported in our previous work [24]. Herein, as extension of our research, we present three new 5-NO_2-ppy-containing iridium(III) complexes [Ir(5-NO_2-ppy)$_2$(PPh_3)(L)] (L = NCO^-, **2**; NCS^-,

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3; N_3^-, **4**. Scheme 1). The electrochemical and photophysical properties of these complexes are elucidated together with **1** to investigate the effect of the introduction of electron-withdrawing substituent nitro to the pyridyl ring in the ppy backbone.

2. Experimental

2.1. Reagents and physical measurements

All reagents were purchased from Aldrich or Alfa Aesar and used as received. All solvents were distilled from the relevant dehydrants under argon atmosphere prior to use. 2-Phenyl-5-nitropyridine (5-NO_2-Hppy) was synthesized using a reported procedure [25]. The dichloro-bridged iridium dimer [Ir(5-NO_2-ppy)$_2$Cl]$_2$ was obtained by the reaction of 5-NO_2-Hppy and $IrCl_3 \cdot H_2O$ according to the available literature [22]. The further reaction of [Ir(5-NO_2-ppy)$_2$Cl]$_2$ and triphenylphosphine resulted in **1** [24].

Elemental analyses were performed on a Yanaco CHN Corder MT-3. IR spectra (4000–400 cm^{-1}) were recorded on a Thermo Nicolet FT/IR-380 spectrophotometer in KBr pellets at room temperature. Electrospray ionization (ESI) mass spectra were carried out with a Thermo Finnigan LCQADVANTAGE MAX mass spectrometer. Ultraviolet and visible spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer at room temperature in dichloromethane solutions with the concentration of 1.0×10^{-5} mol L^{-1}. ^1H NMR measurements were taken on a Bruker AVANCE-500 in chloroform-*d* and chemical shifts were given in ppm relative to tetramethylsilane as an internal reference standard. Solid photoluminescence (PL) spectra were obtained on a Varian Cary Eclipse spectrofluorometer, at the highest spectral resolution, using an excitation wavelength of 320 nm. Spectra were corrected after measurement using the emission calibration obtained from measuring a calibrated lamp spectrum.

2.2. Electrochemical measurements

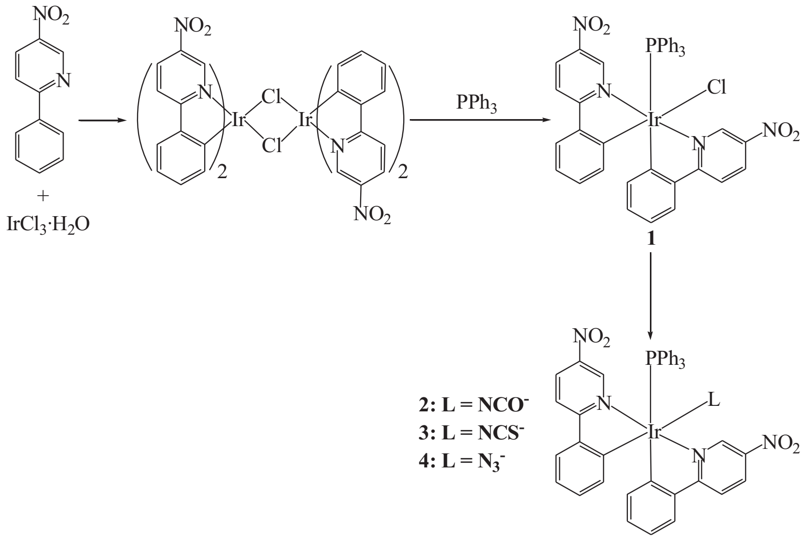
Cyclic voltammetry (CV) measurements were carried out using a Yanaco Polarographic Analyzer P-1100 potentiostat at room temperature. A typical three-electrode configuration was used, where the working electrode was a glassy carbon rod, a platinum wire was used as the counter electrode and Ag/AgCl was the reference electrode. All samples for electrochemical analysis were prepared in acetonitrile being refined in accordance with the standard method at a concentration of 1.0×10^{-3} mol L^{-1}. The supporting electrolyte was tetra-*n*-butyl ammonium hexafluorophosphate (*n*-Bu_4NPF_6) and its concentration was 1.0×10^{-1} mol L^{-1}. The potentials were recorded vs. Ag/AgCl with the ferrocene/ferrocenium (FOC) redox system as an internal standard [26] at a scan rate of 100 mV/s. The scanning scopes were 0.25–2.00 and −1.50–0 V for oxidation and reduction measurements, respectively [27].

2.3. Synthesis of [Ir(5-NO_2-ppy)$_2$(PPh_3)(NCO)] (**2**)

Sodium cyanate (0.0650 g, 1.00 mmol) was added to a solution of **1** (0.1777 g, 0.2 mmol) in 120 mL chloroform and methanol (1:1 v/v). The reaction mixture was then refluxed with stirring for 24 h under argon atmosphere. After the reacted mixture was cooled to room temperature, unreacted sodium cyanate was removed by filtration and evaporating the filtrate led to the crude product. The red crystals of **2** containing two molecules of chloroform, which were suitable for X-ray diffraction analysis, were obtained by recrystallization from chloroform and *n*-hexane (1:3 v/v) in a yield of 0.1859 g (82%). *Anal.* Calc. for **2**·2$CHCl_3$ ($C_{43}H_{31}Cl_6IrN_5O_5P$, 1130.98): C, 45.56; H, 2.76; N, 6.18. Found: C, 45.65; H, 2.72; N, 6.15%. IR (KBr pellet, cm^{-1}): $\nu(C\equiv N)$ 2228; $\nu(C{=}C, C{=}N)$ 1615, 1584, 1568, 1478; $\nu(N = O)$ 1522, 1339; $\nu(P\text{–}C)$ 698. ESI-MS: $m/z = 853$ $(M\text{–}NCO^-)^+$, 591 $(M\text{–}NCO^-\text{–}PPh_3)^+$. ^1H NMR (500 MHz, $CDCl_3$) (ppm): δ 10.17 (s, 1H), 9.80 (s, 1H), 8.48 (d, $J = 5.9$ Hz, 1H), 8.24 (d, $J = 5.7$ Hz, 1H), 8.02 (d, $J = 8.9$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.67–7.63 (m, 2H), 7.31–7.25 (m, 6H), 7.21–7.13 (m, 9H), 6.97 (m, 2H), 6.88 (t, $J = 4.8$ Hz, 1H), 6.63(t, $J = 4.3$ Hz, 1H), 5.93 (d, $J = 8.8$ Hz, 1H), 5.84 (d, $J = 8.2$ Hz, 1H).

2.4. Synthesis of [Ir(5-NO_2-ppy)$_2$(PPh_3)(NCS)] (**3**)

By replacing sodium cyanate with ammonium thiocyanate, the reaction was carried out in a similar method as described in Section 2.3. The red crystals of **3** containing two molecules of chloroform, which were suitable for X-ray diffraction analysis, were acquired by recrystallization from chloroform and *n*-hexane (2:3 v/v) in a yield of 0.1932 g (84%). *Anal.* Calc. for **3**·2$CHCl_3$ ($C_{43}H_{31}Cl_6IrN_5O_4PS$, 1146.96): C, 44.92; H, 2.72; N, 6.09. Found: C, 45.01; H, 2.68; N, 6.12%. IR (KBr pellet, cm^{-1}): $\nu(C\equiv N)$ 2096; $\nu(C{=}C, C{=}N)$ 1617, 1584, 1569, 1479; $\nu(N{=}O)$ 1523, 1339; $\nu(P\text{–}C)$ 698. ESI-MS: $m/z = 853$ $(M\text{–}NCS^-)^+$, 591 $(M\text{–}NCS^-\text{–}PPh_3)^+$. ^1H NMR (500 MHz, $CDCl_3$) (ppm): δ 9.62 (s, 1H), 9.35 (s, 1H), 8.53 (d, $J = 5.2$ Hz, 1H),



Scheme 1. Synthetic procedure of **1**–**4** and their structures.