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Synthesis, characterization, luminescence properties, and DFT calculation of a cationic cyclometalated iridium(III) complex with fluorine-containing phenylquinolinyl and 2,2′-bipyridine ligands

Jia-Yan Qiang [a,b], Ya-Qing Xu [a,b], Bihai Tong [b], Xiu-Fang Ma [b], Qun Chen [a], Wa-Hung Leung [c], Qian-Feng Zhang [a,b,*]

[a] Department of Applied Chemistry, School of Petrochemical Engineering, Changzhou University, Jiangsu 213164, PR China
[b] Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan, Anhui 243002, PR China
[c] Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, PR China

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ABSTRACT

A cationic bis-cyclometalated iridium(III) complex, $[Ir(hfppq)_2(bipy)][PF_6]\cdot 0.5H_2O$ (hfppq = 1,1,1,3,3,3-hexafluoro-2(2-phenylquinolin-4-yl)propan-2-ol, bipy = 2,2′-bipyridine, **1**), was obtained from the reaction of the μ-chloro-bridged dimeric complex $[Ir(hfppq)_2(\mu\text{-}Cl)]_2$ and bipy in the presence of KPF_6. Complex **1** shows a strong emission both in the solid state (ca. 595 nm) and in CH_2Cl_2 solution (ca. 585 nm) at room temperature with the phosphorescence quantum yield of ca. 0.698 and emission lifetime of 0.96 μs. Density functional theory (DFT) calculation was performed on the ground and excited states of complex **1** to provide insight into the structural, electronic, and optical properties of the cationic cyclometalated iridium(III) complex.

1. Introduction

Owing to the strong spin–orbit coupling which can harvest both singlet and triplet excitons for emission, heavy metal–organic complexes are good candidates for organic light-emitting diodes (OLEDs) [1]. Particularly, bis- and tris-cyclometalated (C^N) complexes of iridium(III) based on 2-phenylquinoline and its derivatives have been widely used as one of the promising electroluminescent materials for the OLED technology [2–7]. It is known that the HOMO of the cyclometalated iridium(III) complexes is determined by the 5d orbital of iridium(III) with the π orbitals of the polypyridine ligand and the LUMO is related to the π* orbitals of the diimine ligand [8,9]. For the cationic complexes of bipyridine derivatives, the HOMO primarily resides on the iridium center and the phenyl groups of C^N ligand, the LUMO is mainly located on the N^N ligands [3,10]. Thus, by changing the structures of the ligands, one can modulate the HOMO and LUMO energies of iridium(III) complexes in order to tune the emission colors [11,12]. Notwithstanding, suitable Ir-based materials for the application as OLEDs still need to be further developed.

The main requirements for phosphorescent materials are that phosphorescence should have high color purity and that the phosphorescence quantum yields should be high [13]. With this in mind, we are interested in synthesizing a new sterically hindered fluorinated ligand 1,1,1,3,3,3-hexafluoro-2(2-phenylquinolin4-yl) propan-2-ol (hfppq) and its bis-cyclometalated (C^N) iridium(III) complex $[Ir(hfppq)_2(bipy)]PF_6$. The incorporation of fluorine into the organic molecules may result in profound changes in the physical and chemical properties of the molecules [14]. There also have been several effects of the trifluoromethyl group in the cyclometalated iridium(III) complexes. The first one is the strong electron withdrawing effect on the ligand π-system, which can lower of the HOMO and LUMO energies [15–17], and the second is to provide steric protection around the metal, which is an important parameter for increasing the intensity of the emission [18,19]. In addition, the incorporation of fluorine into the molecule can effectively enhance the stability of the compound. Compared with the similar cationic iridium(III) complexes [7], the present iridium(III) complex, $[Ir(hfppq)_2(bipy)]PF_6$ (bipy = 2,2′-bipyridine), having both a short excited-state lifetime (0.96 μs) and a high phosphorescence yield (0.698), should be advantageous to realization of

* Corresponding author at: Department of Applied Chemistry, School of Petrochemical Engineering, Changzhou University, Jiangsu 213164, PR China. Tel./fax: +86 555 2312041.
E-mail address: zhangqf@ahut.edu.cn (Q.-F. Zhang).

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highly efficient OLEDs. The structural characterization and photoluminescence properties along with theoretical investigations of $[Ir(hfppq)_2(bipy)]PF_6$ are reported in this paper.

2. Experimental

2.1. Materials and measurements

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. All silica gel column chromatography was performed with use of silica gel (200–300 mesh). All reagents, unless otherwise specified, were purchased from Aldrich and were used as received. ^{1}H NMR spectra were recorded on a Bruker ALX Plus 400 spectrometer operating at 400 MHz with tetramethylsilane (TMS) as the internal standard. Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer with use of pressed KBr pellets. Electronic absorption spectra were measured in CH_2Cl_2 solution on a Shimadzu UV-3000 spectrophotometer. Luminescence properties were measured and recorded using an FLS-920 fluorescence spectrometer. Positive-ion ESI mass spectra were recorded on a Perkin-Elmer Sciex API 365 mass spectrometer. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Luminescence lifetime was determined on an Edinburgh FL920 time-correlated pulsed single-photon-counting instrument. Melting point was recorded on an SGW X-4 electrothermal apparatus. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.

2.2. Synthesis of the ligand (Hhfppq)

The ligand Hhfppq was prepared according to procedures described in the literature [13]. Under an atmosphere of nitrogen, Me_3SiCF_3 (854 mg, 6.00 mmol) was charged to a solution of methyl 2-phenylquinoline-4-carboxylate (737 mg, 2.80 mmol) in anhydrous ethylene glycol dimethyl ether (5 mL), and then the mixture was cooled to 0 °C. A catalytic amount of CsF was added to the mixture, and the temperature was slowly warmed to room temperature. After stirring overnight, the hydrolysis was carried out over 3 h by addition of 4 N HCl (4 mL). The resulting product was extracted with ethyl acetate (10 mL × 3). After the removal of solvent, the residue was purified by chromatography on a silica gel column using hexane/ethyl acetate (v:v = 6:1) as an eluent. Yield: 470 mg, 63.8%. m.p.: 203–206 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 8.92 (s, 1H), 8.28 (dd, J = 8.4 Hz, 1H), 8.15 (dd, J = 6.8 Hz, 3H), 7.79 (dd, J = 7.6 Hz, 1H), 7.60 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −73.30 (s). MS ((+)-ESI): m/z = 347 (Calc. 347 for $[C_{16}H_{11}NOF_6]^+$). *Anal.* Calc. for $C_{16}H_{11}NOF_6$: C, 55.34; H, 3.19; N, 4.03. Found: C, 55.23; H, 3.16; N, 4.01%.

2.3. Synthesis of complex $[Ir(hfppq)_2(bipy)][PF_6]\cdot 0.5H_2O$ (**1**)

In a 25 mL rounded-bottomed flask, $IrCl_3\cdot xH_2O$ (40 mg, 0.113 mmol) and ligand Hhfppq (98 mg, 0.283 mmol) were dissolved in a 3:1 v/v mixture of 2-ethoxyethanol and distilled water (12 mL). The mixture was refluxed overnight under nitrogen atmosphere with exclusion of light, and then cooled to the ambient temperature. Bipy (35 mg, 0.224 mmol) was directly added to the reaction solution, and the mixture was stirred for 6 h at room temperature. Addition of an excess KPF_6 (835 mg, 4.54 mmol) in a methanol solution (5 mL) to the reaction solution resulted in formation of the orange solid. The resulting solid product was filtered, and washed with absolute ethanol and dried in vacuum. The orange precipitation was purified by chromatography on a silica gel column using dichloromethane/ethyl acetate (v/v = 2:1) as an eluent. Yield: 52 mg, 37.2%. FT-IR (KBr, cm^{-1}): $\nu(H_2O)$ 3448(br), ν(OH) 3054(s), $\nu([PF_6])$ 835–860(s). ^{1}H NMR (DMSO-d_6, ppm) δ 9.81 (s, 2H), 8.82 (br, 2H), 8.39 (dd, J = 8.0 Hz, 4H), 8.12 (dd, J = 7.2 Hz, 6H), 7.69 (d, J = 6.4 Hz, 2H), 7.51 (m, 4H), 7.28 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 7.2 Hz, 2H), 6.57 (d, J = 7.6 Hz, 2H). ^{31}P NMR (DMSO-d_6, ppm) δ −144.19 (septet, J_{P-F} = 707 Hz). ^{19}F NMR (DMSO-d_6, ppm) δ −69.27 (s), −74.16 (d, J = 708 Hz). MS ((+)-ESI): m/z = 1089 (Calc. 1089 for $[Ir(hfppq)_2(bipy)]^+$). *Anal.* Calc. for $C_{46}H_{28}N_4O_2F_{18}PIr\cdot(H_2O)$: C, 44.45; H, 2.35; N, 4.51. Found: C, 44.27; H, 2.32; N, 4.47%.

2.4. Crystal structure determination

Single crystals of complex **1** were grown from the mixed dichloromethane/–hexane (1:2) solution by slow evaporation at room temperature. The determination of the unit cell and data collection for **1** was performed on a Bruker SMART Apex CCD diffractometer with Mo$K\alpha$ radiation at 296 K using a ω scan mode. The collected frames were processed with the software SAINT [20]. The data were corrected for absorption using the program SADABS [21]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package [22,23]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C_{sp3}–H = 0.96, C_{sp2}–H = 0.93 Å) and included in the structure factor calculations with assigned isotropic displacement parameters, but were not refined. The oxygen atom of water molecule was isotropically refined without hydrogen atoms. Crystal data, data collection parameters and details of the structure refinement are given in Table 1.

2.5. Computational details

The ground state molecular geometries full optimization of the complex was carried out with the density functional theory (DFT) at the Becke3LYP (B3LYP) level [24,25]. Frequency calculations at the same level of theory have also been performed to identify the stationary point as minima (zero imaginary frequency). On the ba-

Table 1
Crystallographic data and experimental details for $[Ir(hfppq)_2(bipy)][PF_6]\cdot 0.5H_2O$ (**1**).

Compound	**1**
Empirical formula	$C_{46}H_{29}N_4O_{2.5}F_{18}PIr$
Formula weight	1242.90
Crystal system	Orthorhombic
a (Å)	26.7123(8)
b (Å)	17.8006(5)
c (Å)	19.9131(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9469.6(5)
Space group	*Pbcn*
Z	8
D_{calc} (g cm^{-3})	1.744
Temperature (K)	296(2)
$F(000)$	7170
μ (Mo-Kα) (mm^{-1})	2.969
Total reflections	75864
Independent reflections	10948
No. of parameters	613
R_{int}	0.0991
R_1[a], wR_2[b] ($I > 2\sigma(I)$)	0.0638, 0.1251
$R1$, $wR2$ (all data)	0.0998, 0.1688
Goodness-of-fit (GOF)[c]	1.040

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR2 = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.
[c] $GOF = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.