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What's the effect of fluorine on properties of Ir(III) complexes?

Effects of fluorine substituent on properties of cyclometalated iridium(III) complexes with a

2,2'-bipyridine ancillary ligand

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Abstract:

Cationic cyclometalated Ir(III) complexes (Ir1-Ir5)with fluorine-substituted 2-phenylpyridine (ppy) derivatives as C^N cyclometalating ligands and 2,2'-bipyridine (bpy) as the ancillary ligand, have been synthesized and fully characterized. The influences of the number and the position of fluorine atoms at the cyclometalating ligands on the photophysical, electrochemical and oxygen sensing properties of the Ir(III) complexes have been investigated systematically. The introduction of fluorine on the C^N cyclometalating ligands of the complexes results in blue-shifts of the maximum emission wavelengths, and increases in the photoluminescence quantum yields (Φ_{PL}), phosphorescence lifetimes and energy gaps, compared non-fluorinated the $[Ir(ppy)_2(bpy)]^+PF_6^-$ (**Ir0**). to Among them, 2-(2,4-difluorophenyl)pyridine-derived Ir4 shows the maximum blue-shift (514 nm vs. 575 nm for and the highest Φ_{PL} (50.8% vs. 6.5% for **Ir0**). The complex **Ir3** with **Ir0**) 2-(4-fluorophenyl)-5-fluoropyridine as C^N ligand exhibits the highest oxygen sensitivity and excellent operational stability in 10 cycles within 4000 s.

Keywords: Fluorine, Ir(III) complex, Photophysical property, Electrochemical property, Oxygen sensitivity.

1. Introduction

Fluorine is a special element with the strongest electronegativity and the atomic radius with the size near to the hydrogen atom.^[1] Its unique electronic structure allows fluorine atoms to structurally modify the molecules by simply replacing the hydrogen atom, thereby effectively adjusting the properties of compounds. Compared with pure organic compounds,^[2-4] phosphorescent heavy-metal complexes based on metal-to-ligand charge-transfer transition (³MLCT) exhibit superior photophysical properties.^[5-7] Among them, cyclometalated iridium(III) complexes, due to relatively long lifetimes, high luminescent quantum yields, flexible tuning of photophysical and electrochemical properties by ligands,^[8, 9] have been often used as highly efficient emitters in organic light-emitting diodes (OLEDs),^[10-18] light-emitting electrochemical cells (LECs),^[19-21] cell imaging,^[22, 23] water redox^[24-27] and phosphorescent chemosensing systems.^[28-30]

In 2008, He et al. synthesized an Ir(III) complex $[Ir(dfppy)_2(pzpy)]^+PF_6^-$ (dfppy = 2-(2,4-difluorophenyl)pyridine, pzpy = 2-(1H-pyrazol-1-yl)pyridine), which demonstrated the bluest light emission (460 nm) in the LEC at that time.^[19] In the same year, $[Ir(dfppy)_2(bpy)]^+PF_6^-$ was prepared by Yu et al. and used as a phosphorescent dye for staining the cytoplasm of living cells.^[22] In 2011, Wang et al. reported that introduction of fluorine substituent at the 6-position of the benzothiazolyl moiety of the 2-phenylbenzothiazole ligand, the corresponding complex (F-bt)₂Ir(acac) exhibited excellent performances of OLEDs.^[31] Very recently, Wang et al. synthesized an Ir(III) complex $[Ir(F_2bpy)_2(ppba)]^+PF_6^-$ (ppba = 4-(6-(1H-pyrazol-1-yl)pyridin-3-yl)

benzaldehyde) by introducing fluorine atoms into the 2 and 6 positions of the bpy. This complex was used as a photosensitizer for photocatalytic water-reduction, providing the hydrogen generation yield up to 312 μ mol in 5 h.^[27] We have a long-standing interest in investigating the structure-property relationship of cyclometalated complexes.^[32-37] In 2015, we found that introduction of fluorine into the cyclometalating ligands strongly improved the photostability of the corresponding cyclometalated Pt(II) complexes.^[38] Recently, we synthesized a fluorinated Ir(III) complex Ir(DPAFppy)₂(acac), which showed an obviously prolonged phosphorescent lifetime and enhanced oxygen sensitivity than that of the non-fluorinated complex Ir(DPAppy)₂(acac).^[36] Thus, the literature reports disclose that fluorine is an interesting and unique substituent for the modification of functional molecules. Therefore, systematical investigation on the effects of the position and the number of the fluorine atoms at the target molecules is of great importance for the design of novel phosphorescent systems with high performances.

In this work, five fluorinated cationic cyclometalated Ir(III) complexes (**Ir1-Ir5**) with 2,2'-bipyridine (bpy) as N^N ancillary ligand were synthesized (**Scheme 1**), which were used to explore the effects of the position and the number of fluorine atoms on the photophysical and electrochemical properties of the corresponding Ir(III) complexes, compared with a non-fluorinated complex **Ir0**. In addition, the oxygen sensitivity and operational stability of the Ir(III) complexes were studied.

2. Results and discussion

2.1 Synthesis and characterization of complexes

Chemical structures of the Ir(III) complexes are shown in **Scheme 1** (the detailed synthetic protocols are shown in **Scheme S1**, see Supporting Information). The cyclometalating ligands **L0-L5** were prepared *via* a palladium-catalyzed ligand-free and aerobic Suzuki-Miyaura reaction in aqueous ethanol developed by our group,^[39] chemical structures of **L0-L5** are shown in **Scheme S2**. Cyclometalated Ir(III) complexes were synthesized in three-steps from the IrCl₃· 3H₂O with the corresponding ligands to form the chloride-bridged dimers initially, followed by treatment with the 2,2'-bipyridine (bpy), and then an anion exchange reaction to obtain the target Ir(III) complexes.^[34, 40]



Scheme 1 Chemical structures of the Ir(III) complexes for this study.

2.2 UV-Visible Absorption Spectra and Emission Spectra

UV-vis absorption spectra of L0-L5 and Ir0-Ir5 in CH_2Cl_2 at room temperature are presented in Fig. 1 and the corresponding photophysical data are given in Table 1. All complexes exhibit intense absorption with high molar extinction coefficients ($\epsilon = 2.92-6.23 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). The intense short wavelength absorption bands in the range of 200-325 nm are primarily due to the spin-allowed intra-ligand (${}^{1}\pi$ - π *) transitions. The weak absorption with lower extinction coefficients absorption bands in the range of 350-450 nm can be assigned to mixing among metal-to-ligand and ligand-to-ligand charge transfer (MLCT/LLCT) together with ligand-centered (${}^{3}\pi$ - π *) transitions.^[41-42]



Fig. 1 UV-Vis absorption spectra of C^N cyclometalating ligands L0-L5 (a) and Ir(III)



complexes Ir0-Ir5 (b) $(10^{-5} \text{ mol/L in CH}_2\text{Cl}_2)$ at room temperature.

Fig. 2 Emission spectra of **Ir0-Ir5** $(10^{-5} \text{ mol/L in } \text{CH}_2\text{Cl}_2)$ at room temperature.

The normalized emission spectra of Ir0-Ir5 in CH₂Cl₂ are shown in Fig. 2. These fluorine-substituted cyclometalated Ir(III) complexes exhibit intense emission bands at 514-575 nm, and the photoluminescence quantum yields were 6.5%, 12.5%, 11.2%, 28.6%, 50.8%, 37.9%, respectively. The results indicate that the introduction of fluorine atoms on the cyclometalating ligands increases the Φ_{PL} of these complexes compared with **Ir0**. When only one fluorine atom is introduced into the 4-position of the phenyl moiety (Ir1, $\Phi_{PL} = 12.5\%$) or the 5-position of the pyridyl ring (Ir2, $\Phi_{PL} = 11.2\%$), the increase in Φ_{PL} is nearly the same, while the Φ_{PL} of the complexes increases markedly with the increase of the number of fluorine atoms. Especially, the 2-(2,4-difluorophenyl)pyridine derived Ir4 ($\Phi_{PL} = 50.8\%$) achieves the highest Φ_{PL} . The introduction of fluorine atoms on the cyclometalating ligands also results in blue-shifts of the maximum emission wavelengths λ_{em}^{max} of Ir(III) complexes. Moreover, the position of the fluorine atoms at the cyclometalating ligands affects the properties of the complexes to different extents. For example, Ir1 with a fluorine atom at the 4-position of the phenyl ring ($\lambda_{em}^{max} = 542$ nm) exhibits a larger blue-shift than that of Ir2 with 5-fluorinated pyridyl ring ($\lambda_{em}^{max} = 567$ nm). The normalized emission spectra of ethylcellulose (EC) films doped with Ir0-Ir5 (0.5 wt%) were also measured (see Fig. S1). As shown in Table 1, the emission maxima of Ir0-Ir5 in EC films are ranging from 485 to 525 nm. Compared with the emission spectra in solution, the emission spectra in EC films of the complexes exhibit a blue-shift due to the rigidochromic effect.^[43]

Complex	λ_{abc}^{a} (nm)	λ_{am}^{b} (nm)	In CH ₂ Cl ₂			
- I			${\varPhi_{ ext{solution}}}^c$	τ ^d (μs)	$k_{\rm r}^{\ c} (10^5 {\rm s}^{-1})$	$k_{\rm nr}^{\ c} (10^5 {\rm s}^{-1})$
Ir0	256(4.58) 268(4.54)	575(CH ₂ Cl ₂)	0.065	0.58	1.13	16.1
	382(0.72)	525(EC film)				
Ir1	253(6.13) 268(6.23)	542(CH ₂ Cl ₂)	0.125	1.14	1.10	7.67
	369(1.01)	502(EC film)				
	260(4 16) 270(4 25)	567(CH ₂ Cl ₂)				
Ir2	212(1.02)	493(EC film)	0.112	0.69	1.62	12.9
	512(1.75)	515(EC film)				
	268(4.70) 308(2.23)	534(CH ₂ Cl ₂)				
Ir3	370(0.59)	476(EC film)	0.286	1.23	2.32	5.81
		503(EC film)				
	250(4.52) 262(4.36)	514(CH ₂ Cl ₂)				
Ir4	301(2,47) $362(0,73)$	462(EC film)	0.508	1.29	3.94	3.81
	501(2.47) 502(0.75)	485(EC film)				
	238(2,65) 262(2,92)	524(CH ₂ Cl ₂)				
Ir5	230(2.03) $262(2.72)$	471(EC film)	0.379	1.01	3.75	6.15
	290(1.09) 303(0.41)	497(EC film)				

Table 1Photophysical data of Ir0-Ir5.

^{*a*} Measured in CH₂Cl₂ at a concentration of 10^{-5} M and extinction coefficients (10^{4} M⁻¹cm⁻¹) are shown in parentheses, the absorption maxima are the values in bold style.

^b The emission maxima are the values in bold style ($\lambda_{exc} = 400$ nm).

^{*c*} The quantum yields ($\Phi_{solution}$) in deoxygenated CH₂Cl₂ were measured with [Ir(ppy)₂(acac)] ($\Phi_{PL} = 0.34$) as a standard, radiative and nonradiative decay rates of k_r and k_{nr} were calculated from k_r = $\Phi_{PL} \times \tau^{-1}$, k_{nr} = $\tau^{-1} - k_r$. ^{*d*} Excitation wavelength: 405 nm; monitor wavelength: the maximum emission wavelength of the corresponding complex in CH₂Cl₂.

Fluorine substituent has a significant influence on phosphorescence lifetimes (**Table 1**). The lifetimes (τ) of Ir(III) complexes in CH₂Cl₂ were measured to be 0.58-1.29 µs at room temperature

(the phosphorescence decay traces of **Ir0-Ir5** illustrated in **Fig. S3**). The lifetimes increase in the following order: **Ir0 < Ir2 < Ir5 < Ir1 < Ir3 < Ir4**. The results show that the substitution of fluorine at the 4-position of the phenyl (**Ir1**, $\tau = 1.14 \,\mu$ s) prolongs the phosphorescence lifetime obviously (**Ir0**, $\tau = 0.58 \,\mu$ s). Introducing a fluorine at the 5-position of the pyridyl or the 2-position of the phenyl of the cyclometalating ligands results in nearly the same phosphorescence lifetimes for **Ir3** (1.23 μ s) and **Ir4** (1.29 μ s). The 2-(3,4,5-trifluorophenyl)pyridine-derived **Ir5** also exhibits a prolonged lifetime (1.01 μ s) compared to **Ir0**. However, introducing a fluorine atom into the 5-position of pyridyl moiety of the C^N ligand gives only a little increased lifetime for **Ir2** (0.69 μ s). The radiative decay rate (k_r) and the nonradiative decay rate (k_{nr}) of the complexes in CH₂Cl₂ were calculated (**Table 1**). **Ir4** shows the longest lifetime (1.29 μ s) and a relatively higher radiative decay rate than other complexes, which is attributed to the 2-(2,4-difluorophenyl)pyridine ligand. These results are useful information for designing novel Ir(III) complexes with a long lifetime.

2.3 Electrochemical properties

The electrochemical behaviors of these Ir(III) complexes were investigated in CH₂Cl₂, the cyclic voltamograms of these Ir(III) complexes are provided in **Fig. S4** and the corresponding data are collected in **Table 2**. The onset oxidation potentials of **Ir0-Ir5** are at 1.27 V, 1.54 V, 1.34 V, 1.68 V, 1.62 V and 1.79 V, respectively. It is found that the introduction of fluorine atoms into the complexes can increase the onset oxidation potentials. Meanwhile, the onset oxidation potentials of the complexes increase with the number of fluorine atoms. The position of the fluorine atoms at

the cyclometalating ligands affects the oxidation potentials of the corresponding complexes. It is clear that **Ir1** with a fluorine at the 4-position of the phenyl ring (1.54 V) exhibits a positive potential than that of **Ir2** with a fluorine at the 5-position of the pyridyl ring (1.34 V), indicating the relative difficulty of oxidation.^[44, 45] The HOMO-LUMO energy gaps are in the order of 2.74 eV(Ir4) > 2.70 eV(Ir5) > 2.68 eV(Ir3) > 2.56 eV(Ir1) > 2.47 eV(Ir2) > 2.45 eV(Ir0), which is consistent with the results of emission spectra illustrated in **Fig. 2**. Specifically, **Ir4** shows the highest energy gaps, which is attributed to the addition of fluorine atoms at 2 and 4 positions of the phenyl ring of the cyclometalating ligand.

Complex	$E_{ox}^{onset \ a}(V)$	E ^{onset} ^a (V)	$E_{\rm HOMO}^{b} (\rm eV)$	E_{LUMO}^{c} (eV)	$E_{\rm g}^{\ d} ({\rm eV})$
Ir0	1.27	-1.18	-5.67	-3.23	2.45
Ir1	1.54	-1.02	-5.94	-3.38	2.56
Ir2	1.34	-1.12	-5.74	-3.28	2.47
Ir3	1.68	-1.00	-6.08	-3.40	2.68
Ir4	1.62	-1.12	-6.02	-3.28	2.74
Ir5	1.79	-0.92	-6.19	-3.48	2.70

Table 2Electrochemical data of Ir0-Ir5.

^{*a*} $\overline{0.1}$ M [Bu₄N]PF₆ in CH₂Cl₂, scan rate 100 mV s⁻¹, measured using a saturated calomel electrode (SCE) as the standard.

 ${}^{b}E_{\text{HOMO}}(\text{eV}) = -\text{e}(4.4 + E_{ox}^{onset}).$

 $^{c}E_{\text{LUMO}}(\text{eV}) = -\text{e}(4.4 + E_{red}^{onset}).$

 $^{d}E_{g} = E_{LUMO} - E_{HOMO}$. HOMO and LUMO denote the highest-occupied molecular orbital and the lowest-unoccupied molecular orbital, respectively.

2.4 Oxygen sensitivity properties

The oxygen sensors using ethylcellulose (EC) as an efficient matrix have been reported.^[46] Herein the oxygen sensitivity of the Ir(III) complexes was also studied in EC films. The relationship between emission intensity and the concentration of oxygen is reflected by a two-site model to fit the curved Stern-Volmer plots (SVPs) in the heterogeneous oxygen sensing films, which can be described as follows (Eq 1).^[32, 34-36, 38, 47]

$$\frac{I}{I_0} = \frac{\tau}{\tau_0} = \frac{f_1}{1 + K_{\text{SV1}} \cdot p_{\text{O}_2}} + \frac{f_2}{1 + K_{\text{SV2}} \cdot p_{\text{O}_2}}$$
Eq 1

In the equation, I_0 and τ_0 are the unquenched luminescent intensity and lifetime in an inert atmosphere. *I* and τ are the corresponding quantities in the presence of oxygen. f_1 and f_2 are the fractions of the total emission for each component ($f_1 + f_2 = 1$). K_{SV1} and K_{SV2} are the Stern-Volmer constants for the two components. p_{O_2} is the partial pressure of oxygen. The weighted quenching constant K_{SV}^{app} ($K_{SV}^{app} = f_1 \cdot K_{SV1} + f_2 \cdot K_{SV2}$) is the guide of the sensitivity of an oxygen sensor, and a higher value of K_{SV}^{app} indicates that the sensor is more sensitive to oxygen.

The dynamic responses of oxygen sensing films were tested against small steps of O_2 partial pressure variation (**Fig. 3** and **Fig. S5**). The Stern-Volmer plots for oxygen sensing films of these Ir(III) complexes immobilized in EC are shown in **Fig. 4**. The fitting results of the O_2 sensing data of these Ir(III) complexes are summarized in **Table S1**.



Fig. 3 Variation of the emission intensity of Ir3 incorporated into EC with the oxygen concentration.



Fig. 4 Stern-Volmer plots of Ir0-Ir5 oxygen sensing films.

The I_0/I_{100} ratio (I_0 and I_{100} represent the detected phosphorescent intensities from a film exposed to 100% N₂ and 100% O₂, respectively) can be used to evaluate the oxygen sensitivity. As the results shown in **Table S1**, the I_0/I_{100} values of the Ir(III) complexes immobilized in EC films are 2.34 (**Ir0**), 2.56 (**Ir1**), 3.00 (**Ir2**), 3.26 (**Ir3**), 2.64 (**Ir4**) and 2.84 (**Ir5**), respectively. The K_{SV}^{app} values of these Ir(III) complexes immobilized in EC films are 0.00269 (**Ir0**), 0.00359 (**Ir1**), 0.00444 (**Ir2**), 0.00542 (**Ir3**), 0.00412 (**Ir4**), 0.00430 (**Ir5**) Torr⁻¹. The **Ir3** immobilized EC film exhibits the highest sensitivity to O_2 at a K_{SV}^{app} value of 0.00542 Torr⁻¹. These results indicate that introducing fluorine atoms into the Ir(III) complexes can improve oxygen sensitivity compared to the non-fluorinated **Ir0**.

2.5 Operational stability and photostability of oxygen sensing films

Reversibility and stability are important factors to influence the overall performance of a sensor. Therefore, the operational stability tests of oxygen sensing films were conducted. It is clear that the emission intensity responses of **Ir3** are fully reversible when the atmosphere varies periodically between 100% N₂ and 100% O₂ in 4000 s (**Fig. 5**). The complete reversibility of the luminescence emission of the oxygen-sensitive films allows stable and continuous monitoring the concentration of oxygen. Additionally, fast response time (6.3 s for switching from N₂ to O₂) and recovery time (8.2 s for switching from O₂ to N₂) were obtained. Thus, the oxygen sensing films of these cationic Ir(III) complexes exhibit complete reversibility with short response times (see **Fig. S6**).



Fig. 5 Reversibility and response time of Ir3 (0.5 wt%) immobilized in EC when cycling from 100% N_2 to 100% O_2 atmosphere.

3. Conclusions

In summary, six cationic cyclometalated Ir(III) complexes (**Ir0-Ir5**) were synthesized and their photophysical, electrochemical and oxygen sensing properties were studied in detail. The results indicate that the number and the position of the fluorine atoms at the cyclometalating ligands significantly affect the properties of the Ir(III) complexes. The introduction of fluorine on the cyclometalating ligands of the Ir(III) complexes makes the maximum emission wavelengths blue-shifts and results in prolonged phosphorescence lifetimes and increases in photoluminescence quantum yields and energy gaps as well. The 2-(2,4-difluorophenyl)pyridine derived **Ir4** achieves the maximum blue-shift (514 nm *vs.* 575 nm for **Ir0**) and the highest photoluminescence quantum yield (50.8%). Furthermore, the fluorinated Ir(III) complexes immobilized ethylcellulose films demonstrate excellent operational stability in oxygen sensing.

4. Experimental

4.1 Materials and instruments

All starting materials were commercially available and used without further purification. The solvents were treated as required prior to use. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Vaian DLG400 or a 500 MHz Bruker AVANCE III Mass spectra were recorded with a MALDI micro MX spectrometer and a LTQ Orbitrap XL spectrometer. UV/Vis absorption spectra were recorded on an HP8453 UV/Vis spectrophotometer. Emission spectra were recorded with a HITACHI F-7000 fluorescence spectrophotometer. Photoluminescence quantum yields were measured relative to [Ir(ppy)₂(acac)] ($\Phi_P = 0.34$ in CH₂Cl₂, under degassed conditions). Phosphorescence lifetimes were measured on an Edinburgh FLS920 Spectrometer. Cyclic voltammograms of the Ir(III) complexes were recorded on an electrochemical workstation (BAS100B/W, USA) at room temperature in a 0.1 M [Bu₄N]PF₆ solution under argon conditions. The phosphorescent intensity responses of sensing films of the Ir(III) complexes were recorded with a F-7000 spectrofluorimeter.

4.2 Synthesis of cyclometalated Ir(III) complexes

Synthetic procedure of ligands L0-L5

A mixture of 2-bromopyridine derivatives (1 mmol), 1.5 equiv. of arylboronic acid, 2 equiv. of K_2CO_3 , Pd(OAc)₂ (1.5 mol%), ethanol/water (3:1 v/v) was stirred at 80 °C in air for the indicated time. The reaction mixture was added to brine (20 mL) and extracted with dichloromethane. The solvent was concentrated under vacuum, and the product was isolated by column chromatography.

Synthetic procedure of Ir(III) complexes Ir0-Ir5

The IrCl₃· $3H_2O$ (0.2 mmol) was reacted with 2.5 equiv. of cyclometalating ligand in a mixture of 2-ethoxyethanol and water (9 mL/3 mL) at 120 °C under nitrogen for 24 h. Upon cooling to room temperature, the suspension was concentrated under vacuum. The solid was completely dried to give the crude cyclometalated Ir(III) chloride-bridged dimer. Without further purification, the dimeric Ir(III) complex reacted subsequently with 3 equiv. of the 2,2'-bipyridine in 2-ethoxyethanol at 120 °C under nitrogen for 24 h. After cooling to room temperature, a 10-fold excess of KPF₆ was added. The reaction mixture was added to water (15 mL) and extracted with dichloromethane. The crude product was purified by column chromatography.

Ir2: an orange solid, yield 85%; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.87 (d, *J* = 8.1 Hz, 2H), 8.36 (dd, *J* = 9.2, 5.5 Hz, 2H), 8.27 (dd, *J* = 11.2, 4.6 Hz, 2H), 8.01 (td, *J* = 9.2, 2.6 Hz, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.83 (d, *J* = 4.7 Hz, 2H), 7.75 - 7.63 (m, 2H), 7.59 (t, *J* = 2.6 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.23 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 164.17, 158.96, 156.47, 155.62, 149.90, 149.17, 142.83, 139.79, 137.40, 131.09, 128.68, 126.90, 125.26, 122.52, 121.32. HRMS (MALDI-TOF, *m*/*z*): calcd for C₃₂H₂₂N₄F₂Ir [M - PF₆]⁺ 693.1442, found 693.1425; calcd for C₂₂H₁₂F₄N₂Ir [M - PF₆ - bpy]⁺ 537.0749, found 537.0938.

Ir3: a yellow solid, yield 68%; ¹H NMR (500 MHz, DMSO- d_6) δ 8.88 (d, J = 8.2 Hz, 2H), 8.37 (dd, J = 9.2, 5.4 Hz, 2H), 8.30 (t, J = 7.9 Hz, 2H), 8.04 (td, J = 8.7, 4.2 Hz, 4H), 7.86 (d, J = 5.3 Hz, 2H), 7.75 - 7.64 (m, 2H), 7.57 (t, J = 2.5 Hz, 2H), 6.91 (td, J = 8.9, 2.5 Hz, 2H), 5.85 (dd, J = 9.3, 2.5 Hz, 2H). ¹³C NMR (126 MHz, DMSO- d_6) δ 163.81, 162.89, 162.87, 161.81, 158.56, 156.56, 155.48, 152.14, 152.10, 150.14, 139.97, 139.41, 137.50, 137.25, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.63, 127.55, 128.80, 127.55, 128.80, 127.55, 128.80, 127.55, 128.80, 127.55, 128.80, 128.55, 128.55, 128.55, 128.55, 128.55, 128.55, 128.55, 128.55, 128.55,

127.27, 127.12, 125.29, 121.47, 121.42, 117.08, 116.94, 109.84, 109.65. HRMS (LTQ, *m/z*): calcd for C₃₂H₂₀F₄N₄Ir [M - PF₆]⁺ 729.1253, found 729.1235.

Ir5: a yellow solid, yield 80%; ¹H NMR (500 MHz, DMSO- d_6) δ 8.91 (d, J = 8.2 Hz, 2H), 8.40 - 8.26 (m, 4H), 8.16 (dd, J = 10.8, 6.4 Hz, 2H), 8.05 (d, J = 5.2 Hz, 2H), 7.96 (dd, J = 11.4, 4.3 Hz, 2H), 7.76 - 7.64 (m, 2H), 7.56 (d, J = 5.7 Hz, 2H), 7.13 (t, J = 6.7 Hz, 2H). ¹³C NMR (126 MHz, DMSO- d_6) δ 165.25, 156.31, 155.26, 154.42, 150.42, 149.62, 148.39, 148.30, 146.48, 146.40, 140.94, 140.52, 140.28, 139.19, 138.53, 138.41, 138.25, 129.36, 125.40, 125.15, 124.20, 120.78, 110.31, 110.17. HRMS (LTQ, m/z): calcd for C₃₂H₁₈F₆N₄Ir [M - PF₆]⁺ 765.1065, found 765.1046.

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Highlights

1) The position and number of fluorine atoms affect properties of cationic Ir(III)

complexes.

2) Fluorinated cationic Ir(III) complexes show increased photoluminescence quantum yields.

3) Fluorinated cationic Ir(III) complexes demonstrate excellent oxygen sensing stability.

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Dear Editor,

There is no conflict of interest to declare for the manuscript "Effects of fluorine substituent on properties of cyclometalated iridium(III) complexes with a 2,2'-bipyridine ancillary ligand".

Sincerely,

Chun Liu

Journal Proposi