Electronic Supplementary Information

Trifluoromethyl-substituted cyclometalated iridium^{III} emitters with

high photostability for continuous oxygen sensing

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Materials and Methods

Unless otherwise noted, all the cross-coupling reactions for preparing the ligands were carried out in air. All reagents and solvents were obtained from Alfa Aesar or Avocado, and the solvents were treated as required prior to use. ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with a MALDI micro MX spectrometer.

UV/Vis absorption spectra were recorded on an HP8453 UV/Vis spectrophotometer. Fluorescence spectra were recorded with a PTI-700 spectrofluorimeter. Luminescent quantum yields were measured with $[Ir(ppy)_2(acac)]$ (UP = 0.34 in CH₂Cl₂, under degassed conditions). Phosphorescence lifetimes were measured on an Edinburgh FLS920 Spectrometer in a degassed dichloromethane solution with excitation wavelength at 410 nm. 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 gas protection. Phosphorescent intensity response of sensing films of the Ir(III) complexes were recorded with a F-7000 spectrofluorimeter. Thermogravimetry analyses (TGA) were carried out using a Perkin-Elmer thermogravimetry analyses at a heating rate of 10 °C min⁻¹ under a nitrogen atmosphere. Density functional theory (DFT) calculations using B3LYP functional were performed. The structures of the Ir(III) complexes were optimized using density functional theory (DFT) with the B3LYP functional and 6-31G(d)/LanL2DZ basis set. The basis set used for C, H, O, N and F atoms was 6-31G while LanL2DZ basis set were employed for iridium atoms. All these calculations were performed with the Gaussian 09 software package.

Synthetic method and characterization of ligands

Ligands L1 – L4: a mixture of 2-pyridyl bromide, 1.5 equiv of arylboronic acid, 2 equiv of K_2CO_3 , Pd(OAc)₂ (1.5 mol%) and ethanol/distilled water (3:1 v/v) was stirred at 80 °C in air for indicated time. The reaction mixture was added to brine (15 mL) and extracted four times with ethyl acetate (4×15 mL). The solvent was concentrated under vacuum, and the product was isolated by short-column chromatography on silica gel (200-300 mesh).

L1-L4 were conveniently synthesized according to the reported method.¹

^{F₃c- \sim **L1:** Yield: 90.2%, a white solid; ¹H NMR (400 MHz, dimethylsulfoxide-*d*₆): $\delta = 9.12$ (s, 1H, Ph), 8.49 – 8.28 (m, 3H, Ph), 8.22 (d, *J* = 8.3 Hz, 1H, Ph), 8.05 (d, *J* = 7.8 Hz, 2H, Ph), 7.88 (d, *J* = 7.9 Hz, 4H, Ph).}

 $F_{3}c \longrightarrow cF_{3}$ L2: Yield: 84.9%; a white solid; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.98$ (s, 1 H, Ph), 8.07 (d, J = 8.1 Hz, 2 H, Ph), 8.16-8.18 (d, J = 8.2 Hz, 1 H, Ph), 7.88-7.91 (d, J = 7.9 Hz, 1 H, Ph), 7.76-7.78 (d, J = 7.8 Hz, 2H, Ph).

L3: Yield: 80.9 %, a white solid; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.95$ (s, 1 H, Ph), 8.03-8.05 (d, J = 8.1 Hz, 2 H, Ph), 7.97-7.99 (d, J = 8.0 Hz, 1 H, Ph), 7.84 (d, J = 7.8 Hz, 1 H, Ph), 7.48-7.53 (m, 3 H, Ph).

 F_3 **C L4:** Yield: 84.5 %, a white solid; ¹H NMR (400 MHz, CDCl₃): δ =8.74 (d, J = 8.7 Hz, 1 H, Ph), 8.11-8.13 (d, J = 8.1 Hz, 2 H, Ph), 7.72-7.83(m, 4 H, Ph), 7.29-7.32(t, J = 7.3 Hz,1 H, Ph).

Synthetic method and characterization of iridium complexes

The targeted Ir(III) emitting materials were obtained according to previously reported method.² IrCl₃·3H₂O and 2.5 equiv. of cyclometalating ligand were added in a 3:1 mixture of 2-ethoxyethanol with water to 110 °C and stirred for 24 h. Upon cooling to room temperature, the yellow precipitate was collected by filtration and washed with water. The wet solid was completely dried to give the crude chloro-bridged dimer complex. Without further purification, the dimer subsequently reacted with 10 equiv. of the chelating diketone derivative and 10 equiv. of Na₂CO₃ in 2-ethoxyethanol at 120 °C for 24 h. The solution was cooled down to room temperature. The crude product was purified by column chromatography over silica using CH₂Cl₂: n-hexane (1:1) as eluent to yield the pure product of the desired iridium complex.

Lx1: Yield 58.1 %, an orange solid; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.79$ (d, J = 1.5 Hz, 2H, Ph), 8.05 (dd, J = 16.6, 5.2 Hz, 4H, Ph), 7.74 (dd, J = 17.9, 12.6 Hz, 10H, Ph), 7.11 (d, J = 7.8 Hz, 2H, Ph), 6.49 (s, 2H), 5.32 (s, 1H, CH), 1.82 (s, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): $\delta = 185.4$, 166.8, 147.8, 147.2, 146.6, 145.6, 139.8, 136.2, 134.5, 130.5, 129.1, 127.3, 126.5, 125.7, 125.7, 122.7, 119.4, 118.5, 118.2, 101.0, 28.8. HRMS(EI): calcd. for C₄₃H₂₇F₁₂IrN₂O₂ [M]⁺ 1024.1510; found 1024.1451.

Lx2: Yield 59.7 %, an orange solid; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.75$ (s, 2H, Ph), 8.06 (d, J = 1.2 Hz, 4H, Ph), 7.71 (d, J = 8.1 Hz, 2H, Ph), 7.13 (d, J = 8.1 Hz, 2H, Ph), 6.38 (s, 2H, Ph), 5.31 (s, 1H, CH), 1.83 (s, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): $\delta = 185.8$, 170.7, 148.4, 146.5, 145.4, 135.0, 133.6, 131.4, 129.5, 125.3, 125.4, 125.1, 122.3, 119.2, 118.7, 101.0, 28.5. HRMS (EI): calcd. For $C_{31}H_{19}F_{12}IrN_2O_2$ [M]⁺872.0884; found 872.0890.

 $\underbrace{\textbf{Lx3}: \text{Yield 54.2 \%, an orange solid; }^{1}\text{H NMR (400 MHz, CDCl_3): } \delta = 8.75}_{\text{(s, 2H, Ph), 7.96 - 7.91 (m, 4H, Ph), 7.60 (d,$ *J*= 7.5 Hz, 2H, Ph), 6.86 (t,*J*= 7.2 Hz, 2H, Ph), 6.77 (d,*J*= 7.2 Hz, 2H, Ph), 6.25 (d,*J* $= 7.5 Hz, 2H, Ph), 5.27 (s, 1H, CH), 1.82 (s, 6H, CH_3). ^{13}\text{C NMR (101 MHz, CDCl_3): } \delta = 185.4, 172.1, 149.3, 145.2, 142.9, 134.2, 133.2, 130.6, 125.4, 121.3, 118.1, 100.8, 28.6. HRMS(EI): calcd. for C₂₉H₂₁F₆IrN₂O₂ [M]⁺736.1136; found 736.1145.$



(d, J = 5.7 Hz, 2H, Ph), 7.95 (d, J = 8.1 Hz, 2H, Ph), 7.88 – 7.83 (m, 2H, Ph), 7.64 (d, J = 8.1 Hz, 2H, Ph), 7.29 (s, 2H, Ph), 7.08 (d, J = 8.7 Hz, 2H, Ph), 6.42 (s, 2H, Ph), 5.27 (s, 1H, CH), 1.82 (s, 6H, CH₃).¹³C NMR (101 MHz, CDCl₃): $\delta = 184.9$, 167.2, 148.4, 146.9, 137.5, 129.9, 128.9, 125.4, 123.5, 122.7, 119.3, 118.0, 100.6, 28.6. HRMS(EI): calcd. for C₂₉H₂₁F₆IrN₂O₂ [M]⁺ 736.1136; found 736.1172.



Figure S1. Thermogravimetric analysis (TGA) curve of the Ir(III) complexes under N_2 .



Figure S2. Cyclic voltammograms of Ir(III) complexes measured in CH_2Cl_2 at a scan rate of 100 mVs⁻¹

Luminescent Oxygen Sensing:

Table S1. Parameters for the O_2 -sensing film of Lx1 with different polymers as the supporting matrix (fitting of the results to the two site model).

Complex ^a	Polymer	f_1^b	f_2^b	$K_{\rm SV1}^{c}$	$K_{\rm SV2}^{\rm c}$	\mathbf{r}^{2d}	$K_{\scriptscriptstyle \mathrm{sv}}^{\scriptscriptstyle \mathrm{app}\;e}$	\mathbf{p}_{O_2}			
Lx1	EC	0.08235	0.91765	0.0073	0.0001	0.98768	0.00670	149.1			
Lx1	IMPES-C	0.10121	0.89879	0.00675	0.0000	0.98801	0.00606	164.5			
Lx1	PS	0.24562	0.75438	0.00235	0.0000	0.98725	0.00177	560.3			
a[dye] = 1.5 mg g ⁻¹ . b Ratio of the two portions of the Ir(III) complexes. c Quenching constant of											
the two	portions.	¹ Determina	tion coe	fficients.	^e Weight	ed quen	ching co	nstant,			
$K_{SV}^{app} = f_1 \cdot K_{SV1} + f_2 \cdot K_{SV2}$. The oxygen partial pressure at which the initial emission											

intensity of the film is quenched by 50% and calculated as $1/K_{SV}^{app}$ 50%, in Torr.



Figure S3. Time trace curves of Lx1 incorporated into different polymers. Dye contents = 1.5 mg g^{-1}



Figure S4. Two-site model plots for the sensing films of the Lx1 incorporated into different polymers. Intensity ratios I_0/Ivs . O₂ partial pressure.

Table S2. Parameters for the O_2 -sensing film of ethyl cellulose with different Lx1 contents (fitting of the results to the two site model).

Lx1/EC(wt %)	f_1^a	f2 ^a	K _{SV1} b	K _{SV2} b	r ^{2c}	$K_{sv}^{app d}$	р ₀₂ е			
0.01	0.18857	0.81143	0.00705	0.0000	0.99003	0.00572	174.0			
0.1	0.89917	0.10083	0.00681	0.0001	0.98839	0.00613	165.1			
0.5	0.93674	0.06326	0.00806	0.0000	0.99128	0.00755	132.2			
1.5	0.91765	0.08235	0.0073	0.0001	0.98768	0.0067	149.1			
2.0	0.91534	0.08466	0.00678	0.0000	0.98901	0.00621	160.9			
5.0	0.89764	0.10236	0.00642	0.0000	0.99100	0.00576	173.6			
10.0	0.79518	0.20482	0.00434	0.0001	0.98810	0.00345	300.0			
aRatio of the	two portions	of the Ir	complexes.	^b Quenching	g constant	of the two	portions.			
^c Determination	coefficients.	^d Weighted	quenching	constant, F	$X_{SV}^{app} = f_1 \cdot$	$K_{SV1} + f_2 \cdot F_2$	SV2. eThe			
oxygen partial pressure at which the initial emission intensity of the film is quenched by 50% and										





Figure S5. Time trace curves the O₂-sensing film of EC with different Lx1 contents.



Figure S6. Two-site model plots for the O_2 -sensing film of EC with different Lx1 contents. Intensity ratios I_0/Ivs . O_2 partial pressure.



Figure S7. The ¹H NMR spectrum of Lx1 in CDCl₃.



Figure S8. The ¹H NMR spectrum of Lx2 in CDCl₃.



Figure S9. The ¹H NMR spectrum of Lx3 in CDCl₃.







Figure S12. The ¹³C NMR spectrum of Lx2 in CDCl₃.









References

1 X. Rao, C. Liu, J. Qiu and Z. Jin, *Org. Biomol. Chem.*, 2012, **10**, 7875-7883. 2 C. Liu, X. Rao, X. Lv, J. Qiu and Z. Jin, *Dyes Pigments.*, 2014, **109**, 13-20.