Electronic Supplementary Information

The Influence of Molecular Structure on Collision Radius for Optical Sensing of Molecular Oxygen Based on Cyclometalated Ir(III) Complexes

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Contents

Ir(ppy)$_3$[1]: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, 3H), 7.65 (d, 3H), 7.58 (t, 3H), 7.53 (d, 3H), 6.87 (dd, 12H).

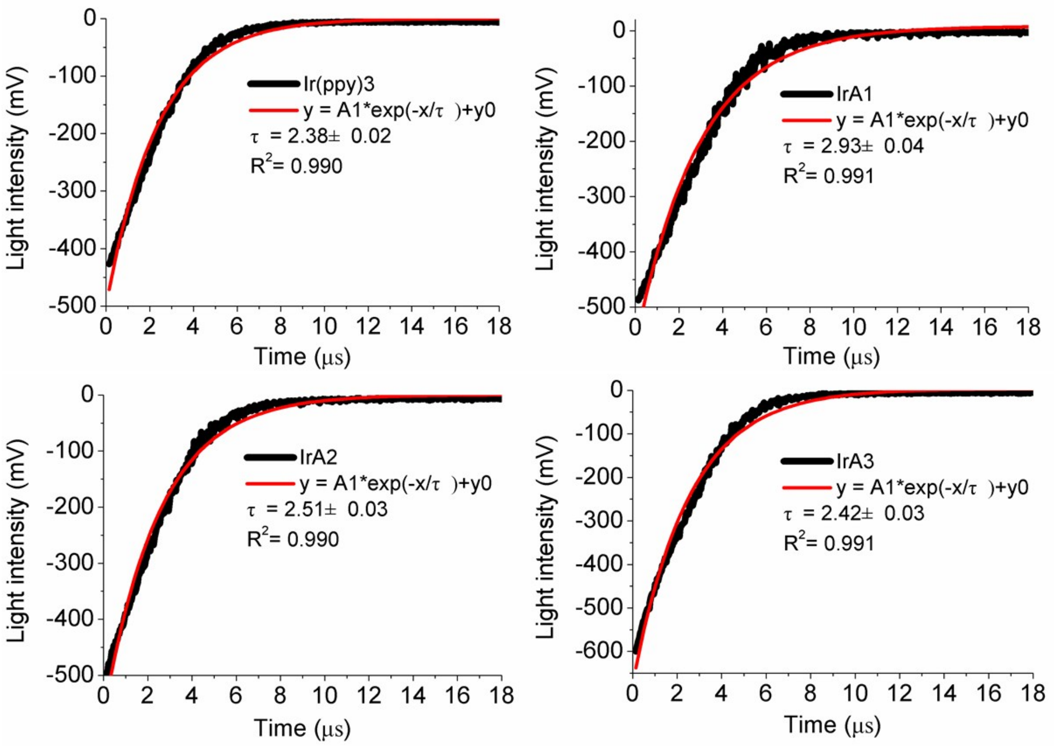


Fig. S1 Phosphorescence emission decay curves of all the Ir(III) complexes in THF in neat N_2. Monoexponential decay regression gave lifetime.

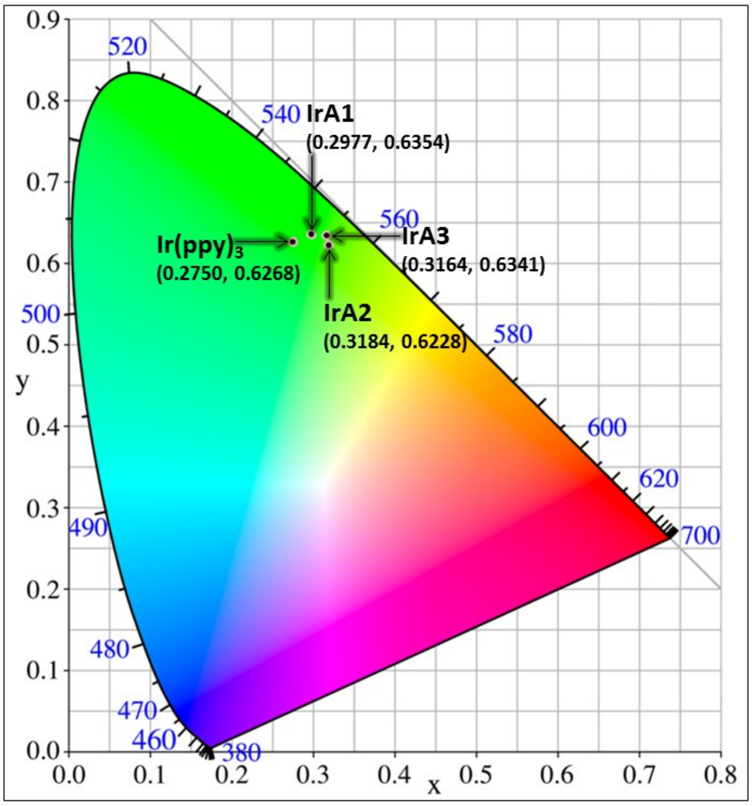


Fig. S2 CIE Plots for IrA1-IrA3 and Ir(ppy)$_3$

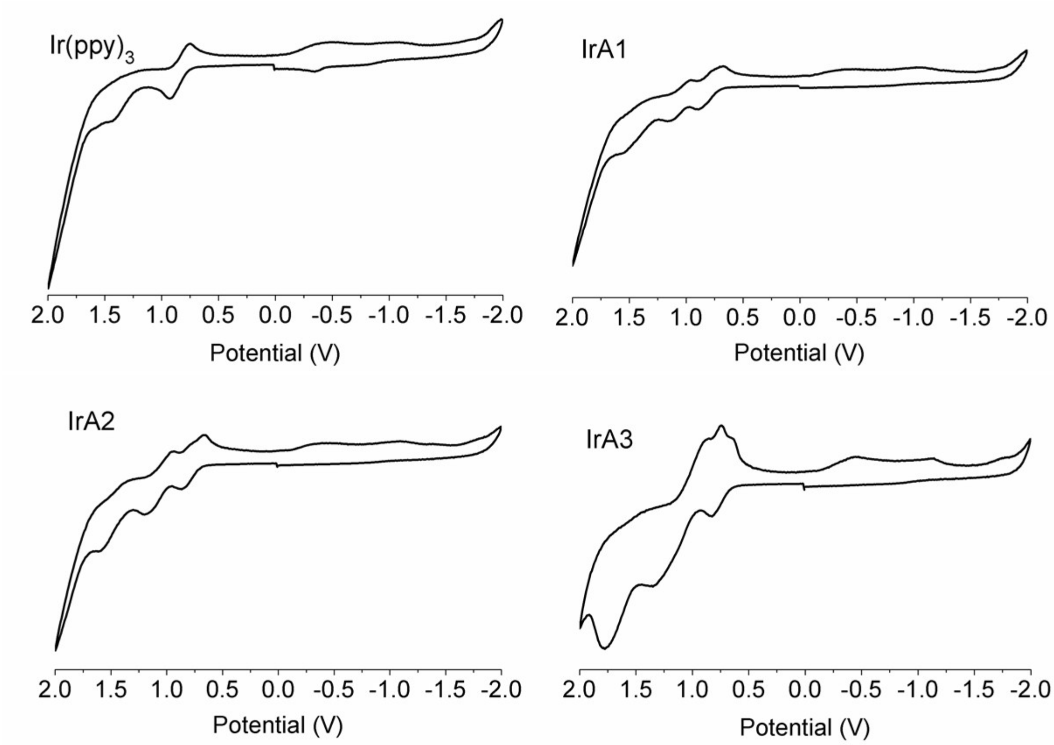
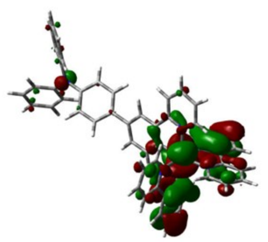
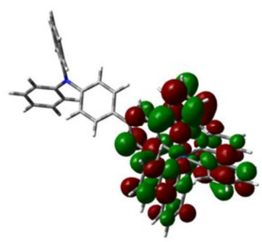


Fig. S3 Cyclic voltammogram of all the Ir(III) complexes. 0.1 M $[Bu_4N]PF_6$ in THF, scan rate 100 mV s^{-1}, measured using saturated calomel electrode (SCE) as the standard.

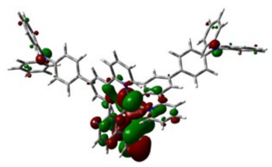
IrA1 HOMO-1 (-5.15 eV)



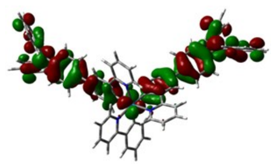
IrA1 LUMO+1 (-1.26 eV)



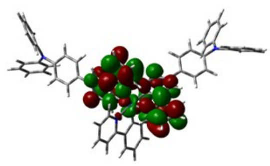
IrA2 HOMO-2 (-5.21 eV)



IrA2 HOMO-1 (-4.83 eV)



IrA2 LUMO+1 (-1.28 eV)



IrA3 HOMO-3 (-5.29 eV)

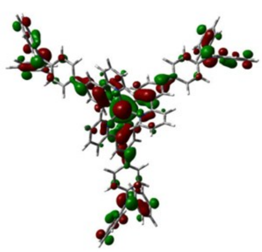


Fig. S4 Molecular orbitals of IrA1-IrA3 and Ir(ppy)$_3$ for the ground state geometry. Calculated by DFT/PCM = THF at the B3LYP/6-31G(d)/LanL2DZ level using Gaussian 16.

Table S1 Frontier orbital energy levels of all the Ir(III) complexes

Ir(III) complexes	HOMO (eV) experimental[a]	LUMO (eV) experimental[b]	E_g (eV) experimental[c]
$Ir(ppy)_3$	-5.24	-2.96	2.28
IrA1	-5.18	-2.89	2.29
IrA2	-5.17	-3.06	2.11
IrA3	-5.18	-3.02	2.16

[a] E_{HOMO} (eV) = -e(4.4 + $E^{1/2}_{ox}$). 0.1 M $[Bu_4N]PF_6$ in THF, scan rate 100 mV s^{-1}, measured using saturated calomel electrode (SCE) as the standard. [b] $E_{LUMO} = E_{HOMO} + E_g$. [c] Estimated from the absorption edge (λ_{edge}) of solid films by equation of $E_g = 1240/\lambda_{edge}$.

Table S2 Parameters for IrA1-IrA3 and $Ir(ppy)_3$; 10^{-5} M in THF on the concentration of O_2 at 0-100%, 25°C. (fitting of the result to the two-site model)

Complexes	λ_{ex}(nm)	λ_{em}(nm)	f_1[a]	f_2[a]	K_{SV1}[b]	K_{SV2}[b]	r^2[c]	K_{SV}^{app}[d]
$Ir(ppy)_3$	400	511	0.985	0.015	121.4	0.00001	0.99983	119.6
IrA1	400	520	0.999	0.001	138.7	0.00001	0.99979	138.6
IrA2	400	522	0.998	0.002	171.7	0.00001	0.99978	171.4
IrA3	400	522	0.998	0.002	205.2	0.00001	0.99985	204.8

[a] Ratio of the two portions of the Ir(III) complexes. [b] Quenching constant of the two portions(bar^{-1}). [c] Determination coefficients. [d] Weighted quenching constant (bar^{-1}).

The limits of detection (LODs) of IrA1-IrA3 and $Ir(ppy)_3$ in THF[2]

Limit of detection (LOD)

$$LOD = \frac{(S/N) \times 10^{-3}}{K_{SV}^{app}}$$

Signal to noise ratio (S/N) $S/N = 20\log\left(U_1/U_0\right)$ U_1: Signal amplitude U_0: Noise amplitude

$Ir(ppy)_3$: U_1 = 511.3, U_0 = 1.3, S/N =51.9, LOD = 0.43 mbar

IrA1: U_1 = 659.9, U_0 = 1.3, S/N = 54.1, LOD = 0.39 mbar

IrA2: U_1 = 502.7, U_0 = 1.3, S/N = 51.8, LOD = 0.30 mbar

IrA3: U_1 = 871.1, U_0 = 1.3, S/N = 56.5, LOD = 0.27 mbar

Table S3 The phosphorescent decay time (τ), emission intensity ratio (I_0/I_{100}-1), and the ratio of collision radiuses ($\sigma/\sigma_{Ir(ppy)3}$) of all the Ir(III) complexes.

Ir(III) complexes	Data	1	2	3	4	5	Mean	Standard
$Ir(ppy)_3$	I_0	511.3	518.6	511.6	532.6	536.4	522.10	10.53
τ_0 (2.38 μs)	I_{100}	6.4	5.9	6.3	6.3	6.0	6.18	0.19
	I_0/I_{100}-1	78.4	86.9	80.6	83.4	88.1	83.48	3.66
IrA1	I_0	659.9	706.8	635.9	675.9	708.6	677.42	27.82
τ_0 (2.93 μs)	I_{100}	5.4	4.9	5.2	5.3	5.0	5.17	0.19
	I_0/I_{100}-1	121.9	144.4	122.1	126.3	141.0	131.13	9.63
	$\sigma_{IrA1}/\sigma_{Ir(ppy)3}$	1.26	1.35	1.22	1.23	1.30	***1.27***	0.05
IrA2	I_0	502.7	524.4	489.4	490.7	509.2	503.28	12.90
τ_0 (2.51 μs)	I_{100}	3.5	3.0	3.5	3.4	3.1	3.30	0.21
	I_0/I_{100}-1	142.2	173.2	136.9	142.5	161.7	151.30	13.82
	$\sigma_{IrA2}/\sigma_{Ir(ppy)3}$	1.72	1.89	1.61	1.62	1.74	***1.72***	0.10
IrA3	I_0	871.1	930.1	900.1	857.4	857.6	883.27	28.12
τ_0 (2.42 μs)	I_{100}	5.1	4.7	4.9	4.9	4.7	4.87	0.15
	I_0/I_{100}-1	169.8	194.4	181.9	174.7	181.8	180.52	8.31
	$\sigma_{IrA3}/\sigma_{Ir(ppy)3}$	2.13	2.20	2.22	2.06	2.03	***2.13***	0.07

References.

1 A. B. Tamayo; B. D. Alleyne; P. I. Djurovich; S. Lamansky; I. Tsyba; N. N. Ho; R. Bau; M. E. Thompson, *J. Am. Chem. Soc.*, 2003, **125**, 7377.

2 X. D. Wang; O. S. Wolfbeis, *Chem. Soc. Rev.*, 2014, **43**, 3666.