Iridium(III) Complexes with Five-Membered Heterocyclic Ligands for Combined Photodynamic Therapy and Photoactivated Chemotherapy

Na Wu, † Jian-Jun Cao,† Xiao-Wen Wu, Cai-Ping Tan,* Liang-Nian Ji and Zong-Wan Mao*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275 (P. R. China), E-mail: cesmzw@mail.sysu.edu.cn; tancaip@mail.sysu.edu.cn

Electronic Supporting Information

Table of Contents

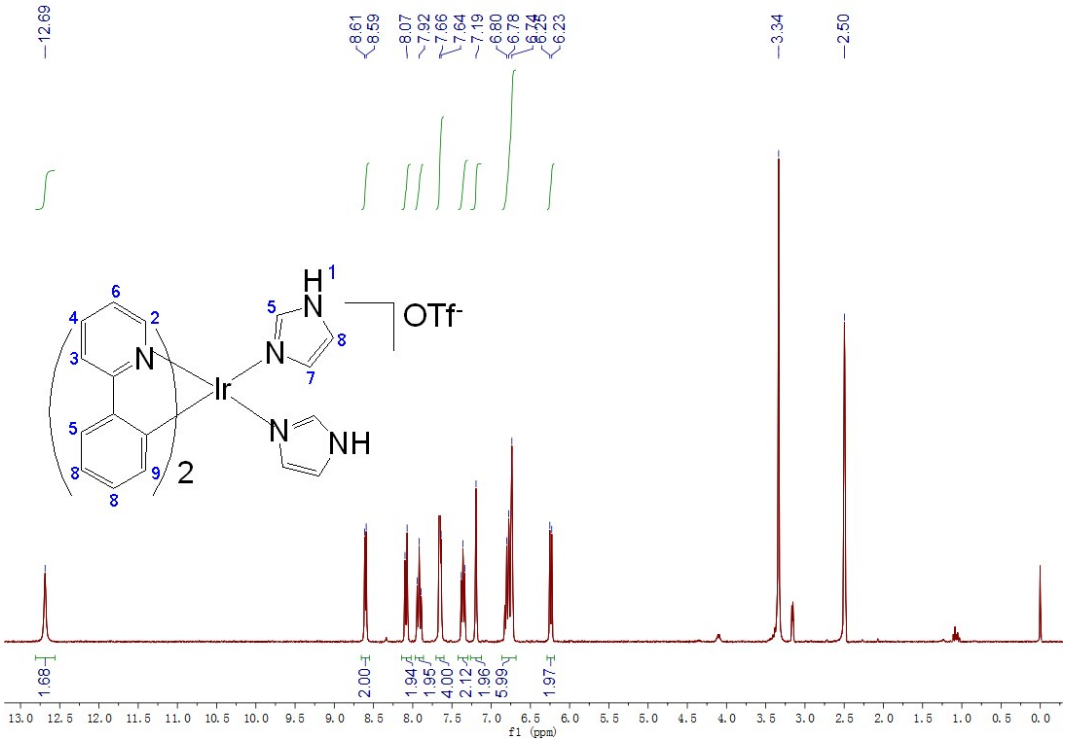

Figure S1 ^{1}H NMR spectrum of complex **Ir1**.

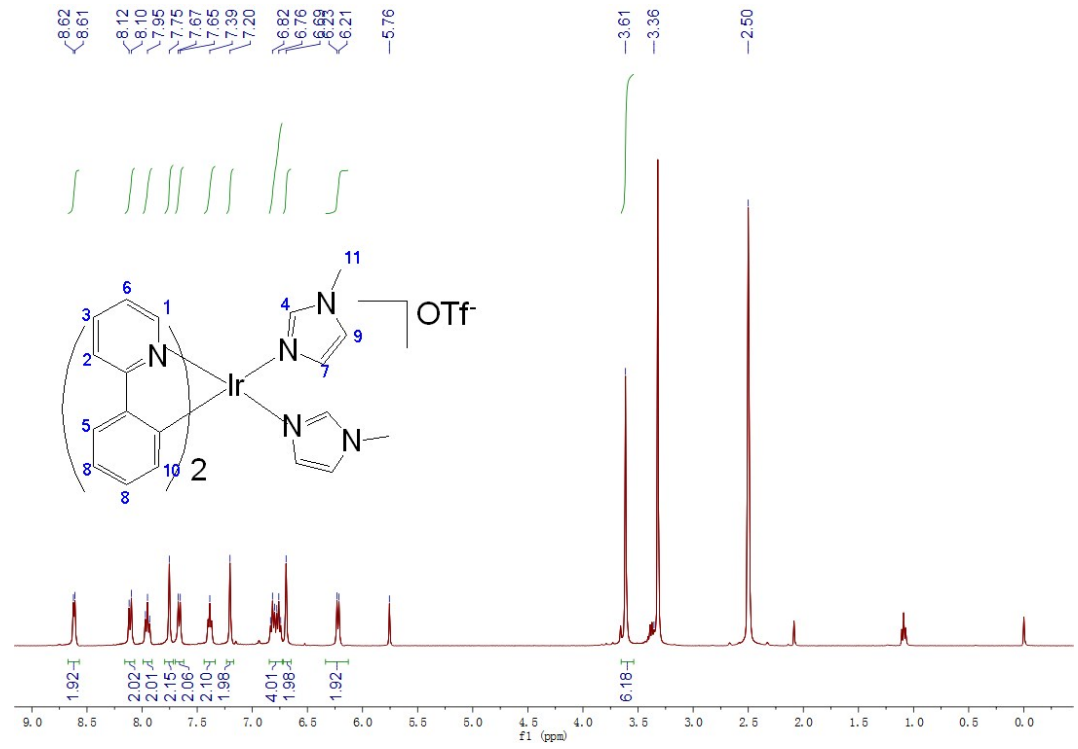

Figure S2 ^{1}H NMR spectrum of complex **Ir2**.

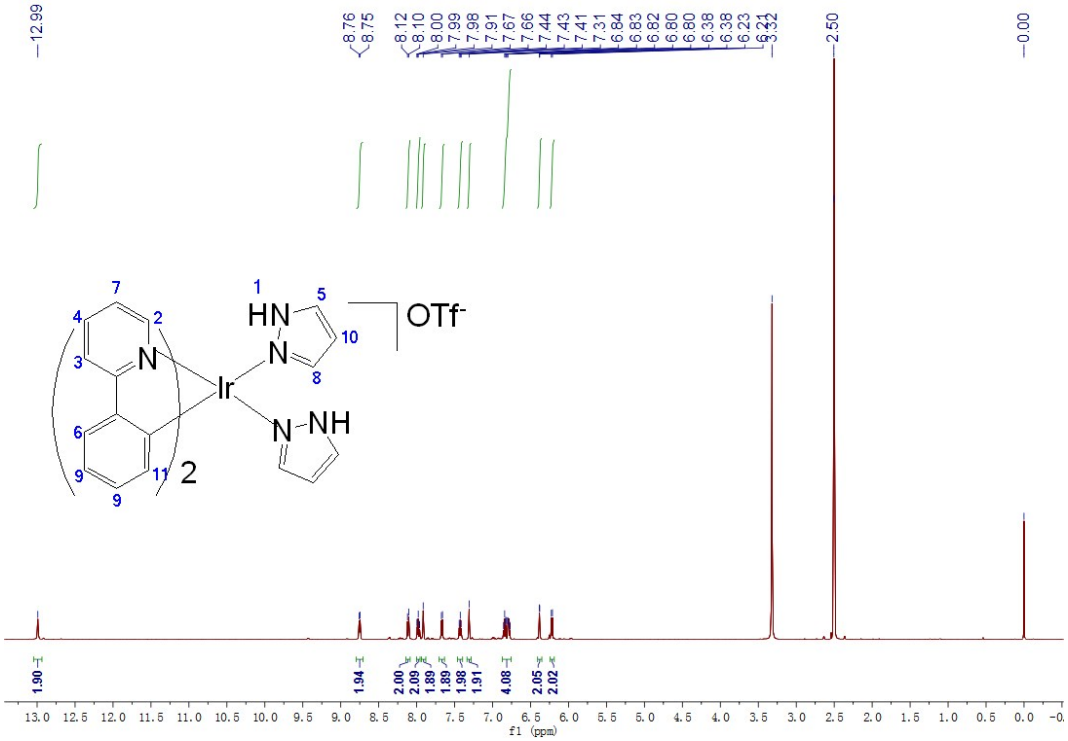

Figure S3 ^{1}H NMR spectrum of complex **Ir3**.

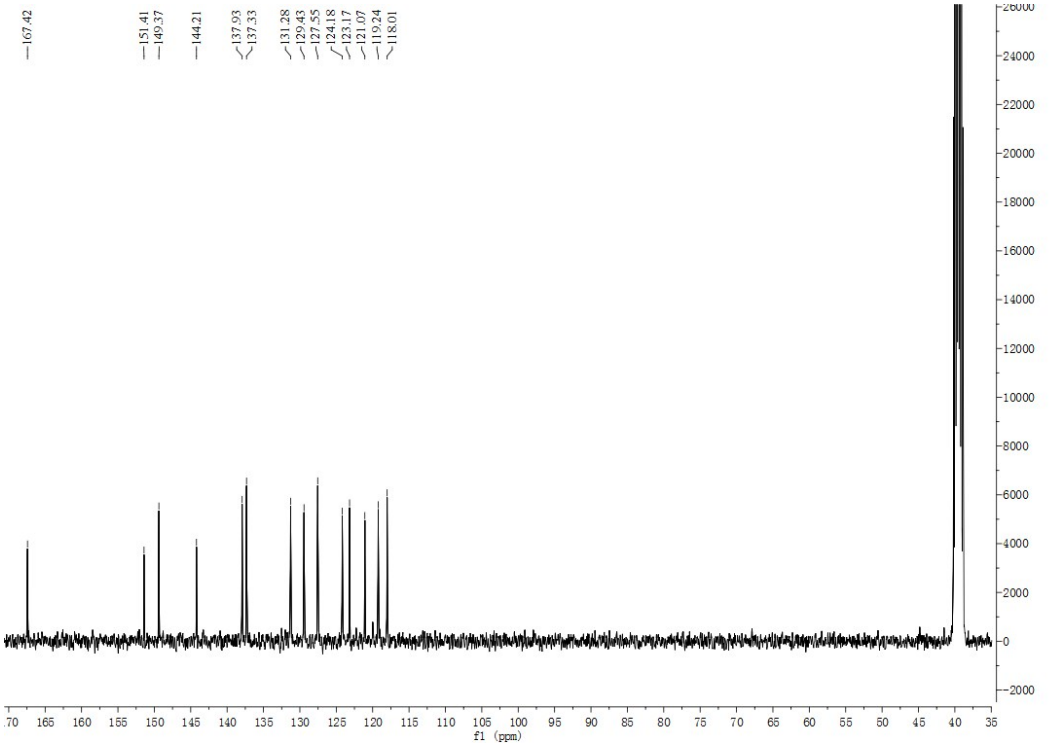

Figure S4 ^{13}C NMR spectrum of complex **Ir1**.

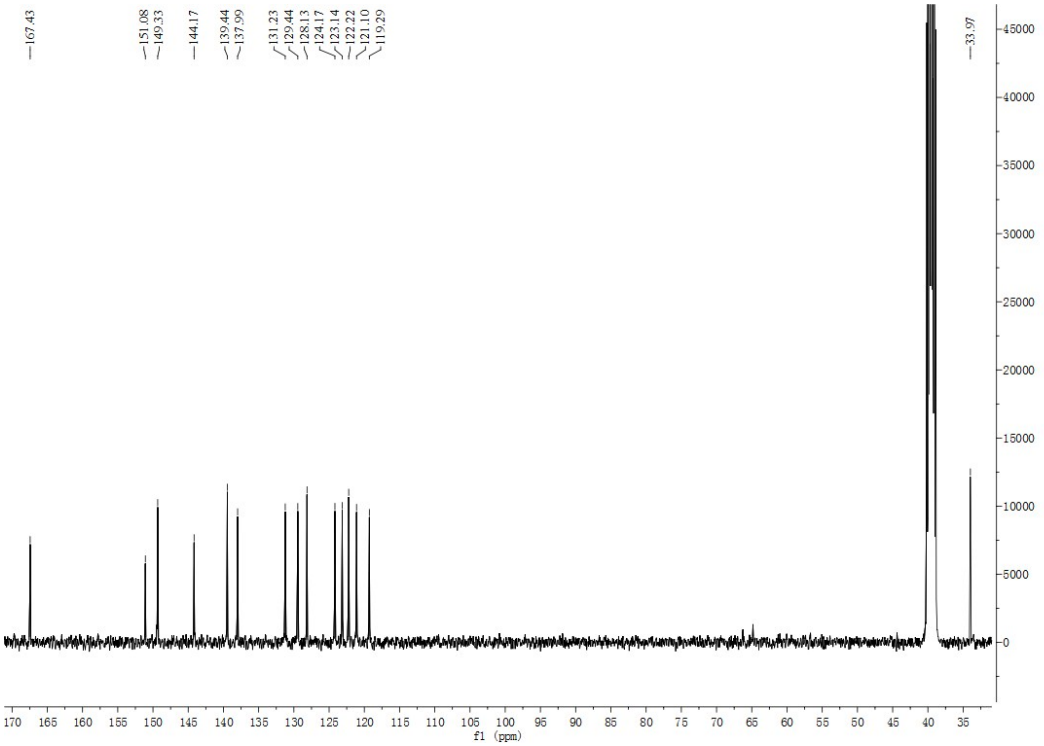

Figure S5 ^{13}C NMR spectrum of complex **Ir2**.

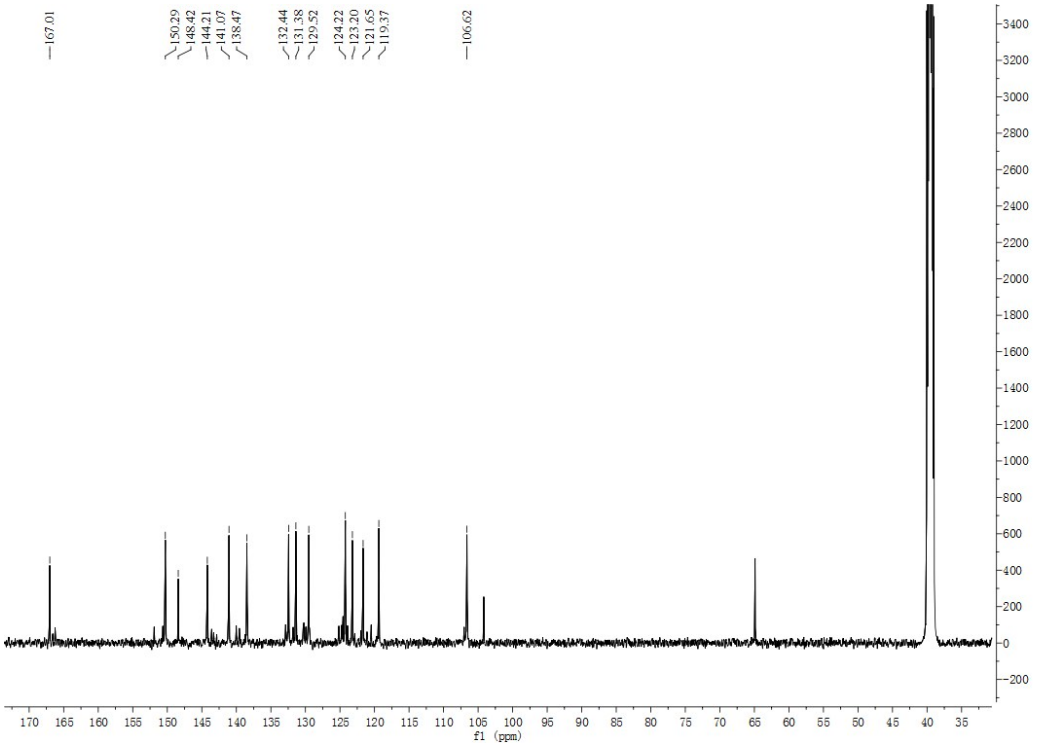

Figure S6 ^{13}C NMR spectrum of complex **Ir3**.

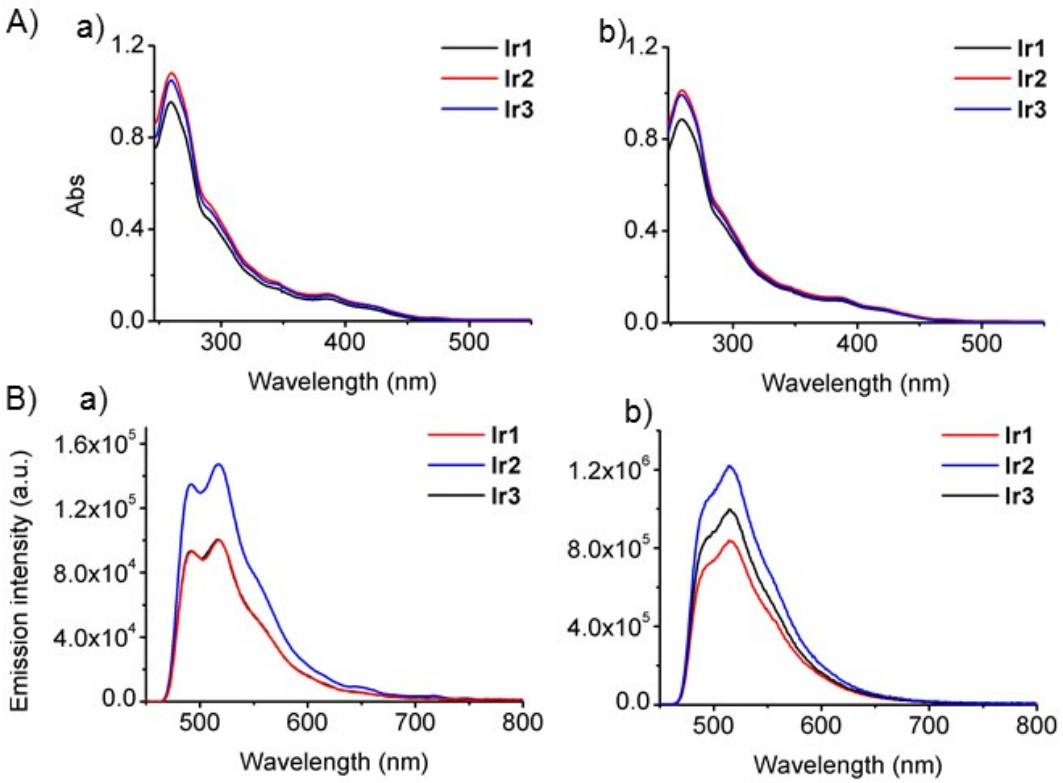

Figure S7 A) UV/Vis spectra of **Ir1**−**Ir3** (3×10^{-5} M) measured in a) CH_3CN and b) PBS at 25 °C. B) Emission spectra of **Ir1**−**Ir3** (3×10^{-5}M) measured in a) CH_3CN and b) PBS at 25 °C.

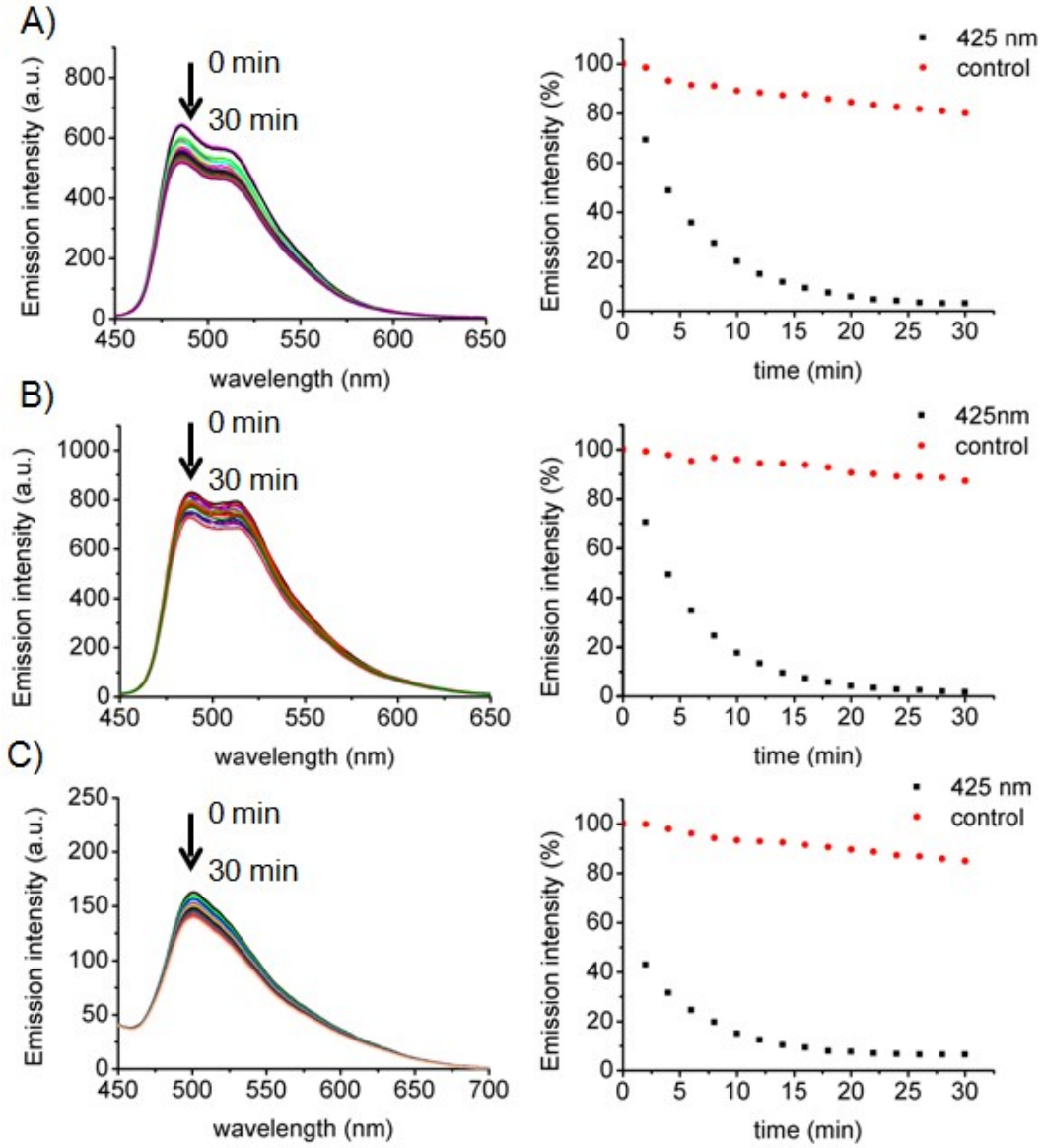

Figure S8 Fluorescence spectra of **Ir1**−**Ir3** (30 μM) upon irradiation with blue light (λ_{irr} = 425 nm, 36 J cm^{-2}). The control samples were kept in dark. A) **Ir1**, B) **Ir2**, C) **Ir3**.

Table S1 Crystal data and structure refinement for **Ir3•**CH_2Cl_2

Compound	**Ir3•**CH_2Cl_2
CDCC no.	1559195
Empirical formula	$C_{28}\ H_{24}\ Ir\ N_6\ 1+,\ C\ F_3\ O_3\ S\ 1-,\ C\ H_2\ Cl_2$
Formula weight	870.73
Temperature	153(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Cmca (Cmce)
Unit cell dimensions	a = 24.0303(3) Å □ α = 90°. b = 15.9300(2) Å β = 90° c = 17.5507(3) Å □ γ = 90°
Volume	6718.45(17) $Å^3$
Z	8
Density (calculated)	1.722 Mg/m^3
Absorption coefficient	10.241 mm^{-1}
F(000)	3408.0
Crystal size	0.220 x 0.190 x 0.180 mm^3
Theta range for data collection	3.679 to 64.932°
Index ranges	-27<=h<=28, -18<=k<=18, -20<=l<=18
Reflections collected	29569
Independent reflections	2932 [R(int) = 0.1485]
Completeness to theta = 64.932°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.04983
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2932 / 63 / 190
Final R indices [I>2sigma(I)][a]	R1 = 0.0780, wR2 = 0.2275
Goodness-of-fit on F^2 [b]	1.074
R indices (all data)	R1 = 0.0837, wR2 = 0.2401
Extinction coefficient	n/a
Largest diff. peak and hole	6.744 and -6.116 $e.Å^{-3}$

$$^{a}R1 = \sum \left| |F_0| - |F_c| \right| / \sum |F_0|, wR2 = \left\{ \sum \left[w\left(F_0^2 - F_c^2\right)^2 \right] / \sum \left[w\left(F_0^2\right)^2 \right] \right\}^{1/2} \quad ^{b}GOF = \left\{ \sum \left[w\left(F_0^2 - F_c^2\right)^2 / (n-p) \right] \right\}^{1/2}$$

where *n* is the number of data and *p* is the number of parameters refined.

Table S2 Selected bond lengths (Å) and bond angles (deg) of **Ir3**

Compound	**Ir3**	
bond lengths (Å)	Ir1–C1	2.008(8)
	Ir1–N1	2.056(7)
	Ir1–N2	2.162(6)
bond angles (deg)	C1–Ir1–C1	87.4(4)
	C1–Ir1–N1	80.1(3)
	C1–Ir1–N1	96.7(3)
	N1–Ir1–N1	175.7(3)
	C1–Ir1–N2	91.6(3)
	C1–Ir1–N2	177.0(3)

Table S3 Photophysical data of complexes **Ir1, Ir2 and Ir3** in degassed medium[a]

Complex	Medium	$\lambda_{abs,\,max}$ (nm)	$\lambda_{em,\,max}$ (nm)	Φ_{em}[b]	τ_{av}[c] (ns)
Ir1	CH_2Cl_2	388	517	0.032	103.7
	CH_3CN	385	518	0.031	42.1
	PBS	379	514	0.051	476.6
Ir2	CH_2Cl_2	388	518	0.026	92.4
	CH_3CN	385	518	0.032	40.2
	PBS	376	511	0.050	488.4
Ir3	CH_2Cl_2	389	518	0.032	88.3
	CH_3CN	387	517	0.042	40.7
	PBS	382	514	0.065	454.5

[a] All emission decays were obtained on freshly prepared samples placed in quartz cuvettes. Samples were 3×10^{-5} M in concentration. [b] Solutions of $[Ru(bpy)_3](PF_6)_2$ were used as the standard, PBS (Φ_{em} = 0.042), CH_3CN (Φ_{em} = 0.062) and CH_2Cl_2 (Φ_{em} = 0.059).[1] [c] Decay curves of compounds were recorded by an Edinburgh FLS 920 Spectrometer. All curves were fitted into a two exponential formula $F(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$;

$$\tau_{ay} = \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}$$

References

[1] K. Nakamaru, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697-2705.