## Electronic Supplementary Information

## Improved Deep-Red Phosphorescence in Cyclometalated Iridium Complexes via Ancillary Ligand Modification

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Index	Page
X-ray crystallographic summary tables	S2–S3
Additional X-ray crystal structures	S4
Additional cyclic voltammograms of complexes	S5–S6
Overlaid UV-vis absorption and excitation spectra	S7–S11
Overlaid room-temperature and 77-K photoluminescence spectra	S12–S16
Time-resolved photoluminescence decay traces	S17–S21
NMR Spectra of complexes	S22-S31

	1c-0.5CH <sub>2</sub> Cl <sub>2</sub>	1d	$2\mathbf{a}\cdot \mathrm{CH}_2\mathrm{Cl}_2$
CCDC	1952045	1952046	1952047
Crystal data		•	
Chemical formula	C46.50H46ClIrN4	$C_{39}H_{40}IrN_5$	$C_{48}H_{43}Cl_2IrN_4S_2$
Mr	888.52	770.96	1003.08
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$
Temperature (K)	173	123	123
<i>a</i> , <i>b</i> , <i>c</i> (Å)	18.501 (3), 9.1561 (16), 26.146 (5)	15.929 (3), 10.934 (2), 19.318 (4)	12.461 (4), 19.090 (6), 17.319 (6)
b (°)	107.620 (4)	107.740 (2)	91.902 (4)
$V(Å^3)$	4221.3 (13)	3204.6 (12)	4118 (2)
m (mm <sup>-1</sup> )	3.26	4.20	3.51
Crystal size (mm)	$0.19 \times 0.17 \times 0.04$	$0.41 \times 0.25 \times 0.19$	$0.33 \times 0.28 \times 0.19$
Data collection			
$T_{\min}, T_{\max}$	0.570, 0.746	0.542, 0.746	0.627, 0.746
No. of measured, independent and observed $[I > 2s(I)]$ reflections	36622, 9330, 7747	19757, 7396, 6784	25770, 9507, 8749
R <sub>int</sub>	0.040	0.027	0.026
(sin q/l) <sub>max</sub> (Å <sup>-1</sup> )	0.641	0.651	0.651
Refinement			
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.039, 0.100, 1.09	0.020, 0.048, 1.04	0.027, 0.075, 1.05
No. of reflections	9330	7396	9507
No. of parameters	494	412	520
No. of restraints	16	0	0
	$w = 1/[s^{2}(F_{o}^{2}) + (0.0474P)^{2} + 7.2873P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$	$w = 1/[s^{2}(F_{o}^{2}) + (0.017P)^{2} + 2.1759P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$	$w = 1/[s^{2}(F_{o}^{2}) + (0.0328P)^{2} + 12.1077P]$ where $P = (F_{o}^{2} + 2F_{c}^{2})/3$
$\Delta \rho_{\text{max}}, \Delta \overline{\rho_{\text{min}}} (e \text{ Å}^{-3})$	1.59, -0.99	0.94, -0.81	0.99, -1.84

Table S1. Summary of crystallographic data for 1c, 1d, and 2a.

	$2\mathbf{b}\cdot\mathbf{C}_{5}\mathbf{H}_{12}$	2d
CCDC	1952048	1952049
Crystal data		
Chemical formula	$C_{50}H_{51}IrN_6S_2$	$C_{35}H_{36}IrN_5S_2$
$M_{ m r}$	992.28	783.01
Crystal system, space group	Triclinic, P <sup>-1</sup>	Monoclinic, C2/c
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.551 (3), 13.444 (4), 15.248 (4)	20.457 (4), 9.7209 (18), 17.889 (3)
a, b, g (°)	111.457 (2), 101.216 (2), 94.278 (2)	90, 117.435 (2), 90
$V(\text{\AA}^3)$	2134.0 (10)	3157.5 (10)
Ζ	2	4
m (mm <sup>-1</sup> )	3.27	4.39
Crystal size (mm)	0.23  imes 0.20  imes 0.17	0.44  imes 0.28  imes 0.10
Data collection		
$T_{\min}, T_{\max}$	0.586, 0.746	0.512, 0.746
No. of measured, independent and observed $[I > 2s(I)]$ reflections	37861, 9724, 9188	9112, 3490, 3402
R <sub>int</sub>	0.027	0.019
(sin q/l) <sub>max</sub> (Å <sup>-1</sup> )	0.649	0.641
Refinement		
$R[F^2 > 2s(F^2)], wR(F^2), S$	0.019, 0.055, 1.22	0.016, 0.040, 1.05
No. of reflections	9724	3490
No. of parameters	538	199
$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} (e \text{ Å}^{-3})$	1.67, -0.85	0.95, -1.01

Table	S2.	Summar	v of c	rvstallog	raphic o	data for	complexes	<b>2b</b>	and 2d
			/						



Figure S1. X-ray crystal structure of 1c, 2b, and 2d. Hydrogen atoms and solvate molecules are omitted for clarity. Ellipsoids are shown at the 50% probability level.



**Figure S2**. Overlaid cyclic voltammograms of complexes 1a-e. CVs were recorded in acetonitrile with 0.1 M NBu<sub>4</sub>PF<sub>6</sub> supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, and currents are low in some of plots because of the limited solubility of some of the compounds in acetonitrile.



**Figure S3**. Overlaid cyclic voltammograms of complexes 2a-d. CVs were recorded in acetonitrile with 0.1 M NBu<sub>4</sub>PF<sub>6</sub> supporting electrolyte, using a glassy carbon working electrode and a scan rate of 0.1 V/s. The arrows indicate the scan direction. Concentrations were not carefully controlled, and currents are low in some of plots because of the limited solubility of some of the compounds in acetonitrile.

		$(E \text{ vs. Fc}^+/\text{Fc}) / \text{V}^a$
$C^N = piq(1)$	$E^{ m red}$	$E^{\mathrm{ox}}$
$L^X = (dmp)_2 Nac Nac^{Me}$ (1a)	-2.22, -2.48	$-0.07^{b}$
$L^X = NacNac^{Me2}$ (1b)	-2.28 $-2.52$	$-0.19^{b}$
$L^X = dipba^{Mes}$ (1c)	-2.24, -2.48	+0.14
$L^X = dipg^{NMe2}$ (1d)	$-2.26, -2.59^{b}$	+0.03
$L^X = (Cy)acNac^{Me}$ (1e)	-2.20, -2.42	+0.24 <sup>b</sup>
$C^N = btp(2)$		
$L^X = (dmp)_2 Nac Nac^{Me}$ (2a)	-2.58 <sup>b</sup>	0.06 <sup>b</sup>
$L^X = NacNac^{Me2}$ (2b)	-2.62 <sup>b</sup>	-0.17
$L^X = dipba^{Mes}$ (2c)	-2.57 <sup>b</sup>	0.23
$L^X = dipg^{NMe2}$ (2d)	$-2.60^{b}$	0.12

Table S3. Summary of cyclic voltammetry data recorded in MeCN solution.

<sup>a</sup> Experiments were performed in acetonitrile solvent with 0.1 M NBu<sub>4</sub>PF<sub>6</sub> electrolyte with scan rate of 0.1 V/s using a glassy carbon working electrode and a silver wire pseudo-reference electrode. Potentials are referenced against the ferrocene/ferrocenium redox couple. <sup>b</sup> Observed wave is irreversible, and the respective  $E_{p,c}$  or  $E_{p,a}$  peak potential is reported.



Figure S4. Excitation spectrum of  $Ir(piq)_2[(dmp)_2NacNac^{Me}]$  (1a), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 660$  nm for the excitation spectrum.



Figure S5. Excitation spectrum of  $Ir(piq)_2(NacNac^{NMe2})$  (1b), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 707$  nm for the excitation spectrum.



**Figure S6.** Excitation spectrum of  $Ir(piq)_2(dipba^{mes})$  (1c), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 661$  nm for the excitation spectrum.



Figure S7. Excitation spectrum of  $Ir(piq)_2(dipg^{NMe2})$  (1d), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 683$  nm for the excitation spectrum.



Figure S8. Excitation spectrum of  $Ir(piq)_2[(Cy)acNac^{Me}]$  (1e), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 657$  nm for the excitation spectrum.



**Figure S9.** Excitation spectrum of  $Ir(btp)_2[(dmp)_2NacNac^{Me}]$  (2a), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 624$  nm for the excitation spectrum.



Figure S10. Excitation spectrum of  $Ir(btp)_2(NacNac^{NMe2})$  (2b), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 633$  nm for the excitation spectrum.



Figure S11. Excitation spectrum of  $Ir(btp)_2(dipba^{mes})$  (2c), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 619$  nm for the excitation spectrum.



Figure S12. Excitation spectrum of  $Ir(btp)_2(dipg^{NMe2})$  (2d), overlaid with its normalized absorption spectrum. Spectra were recorded in THF at room temperature, with  $\lambda_{em} = 626$  nm for the excitation spectrum.



**Figure S13.** Emission spectrum of  $Ir(piq)_2[(dmp)_2NacNac^{Me}]$  (1a), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S14.** Emission spectrum of  $Ir(piq)_2(NacNac^{NMe2})$  (1b), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S15.** Emission spectrum of  $Ir(piq)_2(dipba^{mes})$  (1c), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S16.** Emission spectrum of  $Ir(piq)_2(dipg^{NMe2})$  (1d), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S17.** Emission spectrum of  $Ir(piq)_2[(Cy)acNac^{Me}]$  (1e), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S18.** Emission spectrum of  $Ir(btp)_2[(dmp)_2NacNac^{Me}]$  (2a), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S19.** Emission spectrum of  $Ir(btp)_2(NacNac^{NMe2})$  (2b), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S20.** Emission spectrum of  $Ir(btp)_2(dipba^{mes})$  (**2c**), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



**Figure S21.** Emission spectrum of  $Ir(btp)_2(dipg^{NMe2})$  (2d), recorded at room temperature (298 K) in THF (blue, squares) and at low temperature (77 K) in toluene (red, circles), with  $\lambda_{ex} = 420$  nm.



Figure S22. Photoluminescence decay trace for complex 1a, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S23.** Photoluminescence decay trace for complex **1b**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S24.** Photoluminescence decay trace for complex **1c**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S25.** Photoluminescence decay trace for complex **1d**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S26.** Photoluminescence decay trace for complex **1e**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S27.** Photoluminescence decay trace for complex **2a**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S28.** Photoluminescence decay trace for complex **2b**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S29.** Photoluminescence decay trace for complex **2c**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S30.** Photoluminescence decay trace for complex **2d**, recorded in THF at room temperature with 390-nm excitation. The raw decay trace is shown in black, with the best-fit line displayed in red.



**Figure S31.** <sup>1</sup>H NMR spectrum of ancillary ligand [(Cy)acNac<sup>Me</sup>]H, recorded at 400 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual CH<sub>2</sub>Cl<sub>2</sub> and acetone are marked.



**Figure S32.** <sup>1</sup>H NMR spectrum of Ir(piq)<sub>2</sub>[(dmp)<sub>2</sub>NacNac<sup>Me</sup>] (**1a**), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signal for residual CH<sub>2</sub>Cl<sub>2</sub> is marked.



**Figure S33.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(piq)_2[(dmp)_2NacNac^{Me}]$  (1a), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signal for CH<sub>2</sub>Cl<sub>2</sub> is marked.



**Figure S34.** <sup>1</sup>H NMR spectrum of  $Ir(piq)_2(NacNac^{NMe2})$  (1b), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual  $CH_2Cl_2$  and pentane are marked.



**Figure S35.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(piq)_2(NacNac^{NMe2})$  (1b), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual pentane are marked.



**Figure S36.** <sup>1</sup>H NMR spectrum of  $Ir(piq)_2(dipba^{mes})$  (1c), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, and pentane are marked.



**Figure S37.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(piq)_2(dipba^{mes})$  (1c), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis.



**Figure S38.** <sup>1</sup>H NMR spectrum of  $Ir(piq)_2(dipg^{NMe2})$  (1d), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual CH<sub>2</sub>Cl<sub>2</sub> and pentane are marked.



**Figure S39.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(piq)_2(dipg^{NMe2})$  (1d), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual pentane are marked.



**Figure S40.** <sup>1</sup>H NMR spectrum of Ir(piq)<sub>2</sub>[(Cy)acNac<sup>Me</sup>] (1e), recorded at 400 MHz in CD<sub>2</sub>Cl<sub>2</sub>. Peak positions are shown below the horizontal axis.



**Figure S41.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(piq)_2[(Cy)acNac^{Me}]$  (1e), recorded at 126 MHz in CD<sub>2</sub>Cl<sub>2</sub>. Peak positions are shown below the horizontal axis.



**Figure S42.** <sup>1</sup>H NMR spectrum of Ir(btp)<sub>2</sub>[(dmp)<sub>2</sub>NacNac<sup>Me</sup>] (**2a**), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signal for residual CH<sub>2</sub>Cl<sub>2</sub> is marked.

![](_page_27_Figure_0.jpeg)

**Figure S43.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(btp)_2[(dmp)_2NacNac^{Me}]$  (**2a**), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual CH<sub>2</sub>Cl<sub>2</sub> is marked.

![](_page_27_Figure_2.jpeg)

**Figure S44.** <sup>1</sup>H NMR spectrum of  $Ir(btp)_2(NacNac^{NMe2})$  (**2b**), recorded at 400 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signal for residual toluene is marked.

![](_page_28_Figure_0.jpeg)

**Figure S45.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(btp)_2(NacNac^{NMe2})$  (**2b**), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual toluene is marked.

![](_page_28_Figure_2.jpeg)

**Figure S46.** <sup>1</sup>H NMR spectrum of  $Ir(btp)_2(dipba^{mes})$  (**2c**), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual pentane are marked.

![](_page_29_Figure_0.jpeg)

**Figure S47.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(btp)_2(dipba^{mes})$  (**2c**), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis.

![](_page_29_Figure_2.jpeg)

**Figure S48.** <sup>1</sup>H NMR spectrum of  $Ir(btp)_2(dipg^{NMe2})$  (**2d**), recorded at 600 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual CH<sub>2</sub>Cl<sub>2</sub>, tetrahydrofuran (THF), benzene, and moisture (H<sub>2</sub>O) from NMR solvent are marked.

![](_page_30_Figure_0.jpeg)

**Figure S49.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of  $Ir(btp)_2(dipg^{NMe2})$  (**2d**), recorded at 151 MHz in CDCl<sub>3</sub>. Peak positions are shown below the horizontal axis. Signals for residual pentane, acetone, and CH<sub>2</sub>Cl<sub>2</sub> are marked.