ESI to accompany:

**Red emitting [Ir(C\(^\text{N}\))\(_2\)(N\(^\text{N}\))]\(^+\) complexes employing bidentate 2,2':6,2''-terpyridine ligands for light-emitting electrochemical cells**

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**Fig. S1.** Structure of one of two independent [Ir(ppy)\(_2\)(tpy)]\(^+\) cations in 4{[Ir(ppy)\(_2\)(tpy)][PF\(_6\)]} \(\cdot\) 2.5Et\(_2\)O \(\cdot\) 1.5MeCN \(\cdot\) 3H\(_2\)O. Ellipsoids plotted at 30% probability level; H atoms omitted. Selected bond lengths: Ir1a–N1a = 2.130(5), Ir1a–N2a = 2.214(5), Ir1a–C27a = 1.994(6), Ir1a–C16a = 2.018(6), Ir1a–N5a = 2.042(5), Ir1a–N4a = 2.049(5) Å.

**Fig. S2.** Structure of one of two independent [Ir(ppy)\(_2\)(2)]\(^+\) cations in 4{[Ir(ppy)\(_2\)(2)][PF\(_6\)]} \(\cdot\) Et\(_2\)O \(\cdot\) 2MeCN. Ellipsoids plotted at 30% probability level; H atoms omitted. Selected bond lengths: Ir1a–C23a = 1.996(3), Ir1a–C34a = 2.015(3), Ir1a–N4a = 2.039(2), Ir1a–N5A = 2.058(2), Ir1a–N1a = 2.018(6), Ir1a–N5a = 2.042(5), Ir1a–N4a = 2.049(5) Å.
Fig. S3. Structure of the [Ir(ppy)$_2$(3)]$^+$ cation in 2[[Ir(ppy)$_2$(3)][PF$_6$]]MeCN-H$_2$O with ellipsoids plotted at 30% probability level; H atoms omitted. Selected bond lengths: Ir1–C23 = 2.0037(12), Ir1–C34 = 2.0140(14), Ir1–N5 = 2.0504(12), Ir1–N4 = 2.0533(11), Ir1–N1 = 2.1291(11), Ir1–N2 = 2.2300(10) Å.

Fig. S4. Structure of the [Ir(ppy)$_2$(4)]$^+$ cation in [Ir(ppy)$_2$(4)][PF$_6$]2CH$_2$Cl$_2$ with ellipsoids plotted at 30% probability level; H atoms except those in the NH$_2$ unit are omitted. Selected bond lengths: Ir1–C33 = 2.012(5), Ir1–C22 = 2.013(5), Ir1–N6 = 2.039(4), Ir1–N5 = 2.057(4), Ir1–N1 = 2.153(4), Ir1–N2 = 2.204(4) Å.
Fig. S5. Structure of one of two independent \([\text{Ir}(ppy)_2(ptypy)]^+\) cations in 2\{[\text{Ir}(ppy)_2(ptypy)]\text{[PF}_6\text{]}\}-\text{Et}_2\text{OCH}_2\text{Cl}_2\). Ellipsoids plotted at 30% probability level and H atoms omitted. Selected bond lengths: Ir1b–C32b = 1.929(17), Ir1b–C21b = 1.978(15), Ir1b–N5b = 2.034(13), Ir1b–N6b = 2.043(13), Ir1b–N1b = 2.115(12), Ir1b–N2b = 2.214(14) Å.

Fig. S6. Structure of the \([\text{Ir}(dmppz)_2(tpy)]^+\) cation in \([\text{Ir}(dmppz)_2(tpy)]\text{[PF}_6\text{]}\) with ellipsoids plotted at 30% probability level and H atoms omitted. Selected bond lengths: Ir1–C16 = 2.0030(19), Ir1–C27 = 2.011(2), Ir1–N6 = 2.0250(17), Ir1–N4 = 2.0281(18), Ir1–N1 = 2.1402(17), Ir1–N2 = 2.2212(17) Å.
Fig. S7. Structure of the \([\text{Ir}(\text{dmppz})_2(\text{pytpy})]^+\) cation in \([\text{Ir}(\text{dmppz})_2(\text{pytpy})][\text{PF}_6]\)\(\cdot\)CH\(_2\)Cl\(_2\); ellipsoids plotted at 30% probability level and H atoms omitted. Selected bond lengths: Ir1–C21 = 2.008(3), Ir1–C32 = 2.015(2), Ir1–N7 = 2.031(2), Ir1–N5 = 2.051(2), Ir1–N1 = 2.134(2), Ir1–N2 = 2.206(2) Å.

Fig. S8  500 MHz \(^1\text{H}\) NMR spectrum of \([\text{Ir}(\text{dmppz})_2(\text{Mepytpy})][\text{PF}_6]\)_2 (CDCl\(_3\), 295 K). Peaks marked ** and * are residual CHCl\(_3\) and H\(_2\)O respectively.
Fig. S9. Structure of the [Ir(dmppz)$_2$(Mepytpy)]$^{2+}$ cation in [Ir(dmppz)$_2$(Mepytpy)][PF$_6$]$_2$·2CH$_2$Cl$_2$; ellipsoids plotted at 30% probability level and H atoms omitted. Selected bond lengths: Ir1–C33 1.991(5), Ir1–N5 = 2.018(5), Ir1–C22 = 2.024(5), Ir1–N7 = 2.044(4), Ir1–N1 = 2.152(4), Ir1–N2 = 2.214(4) Å.

Fig. S10. Sweep to positive potential in the cyclic voltammograms of (a) [Ir(ppy)$_2$(2)][PF$_6$] and (b) [Ir(dmppz)$_2$(tpy)][PF$_6$] (with respect to Fc/Fc$^+$; CH$_2$Cl$_2$ solution) showing the quasi-reversible process.
Fig S11. The device performance of the [Ir(ppy)$_2$(6-Phbpy)][PF$_6$] under the pulsed driving conditions, analogous to those used for the best performing devices in this paper. (a) Luminance, and (b) average voltage versus time.

Fig. S12. Photoluminescence spectra in thin films (iTMC:IL 4:1).