

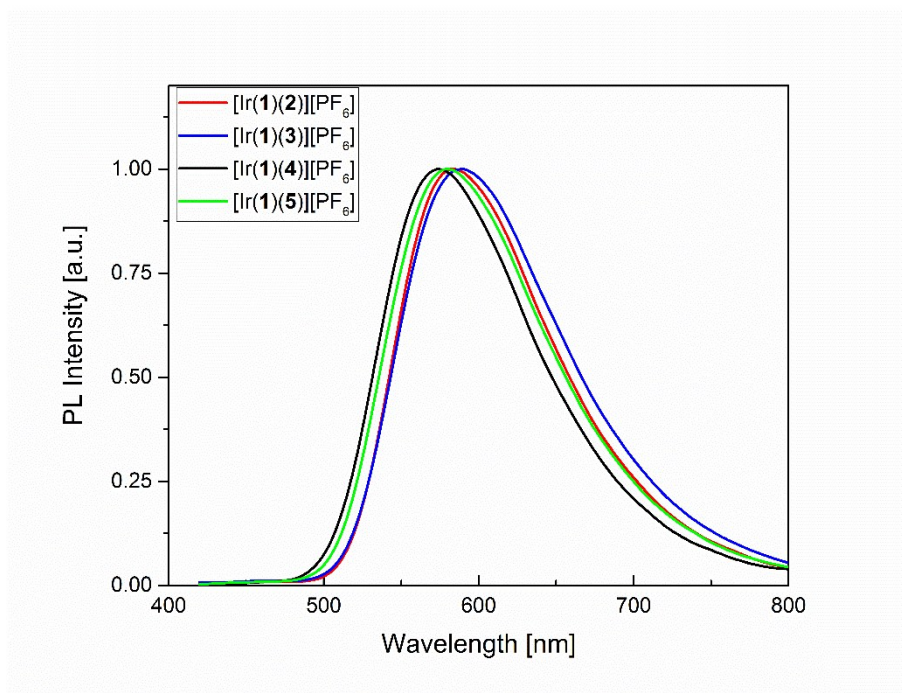
Electronic Supporting Information

**[Ir(C<sup>^</sup>N)<sub>2</sub>(N<sup>^</sup>N)]<sup>+</sup> emitters containing a naphthalene unit within a linker  
between the two cyclometallating ligands**

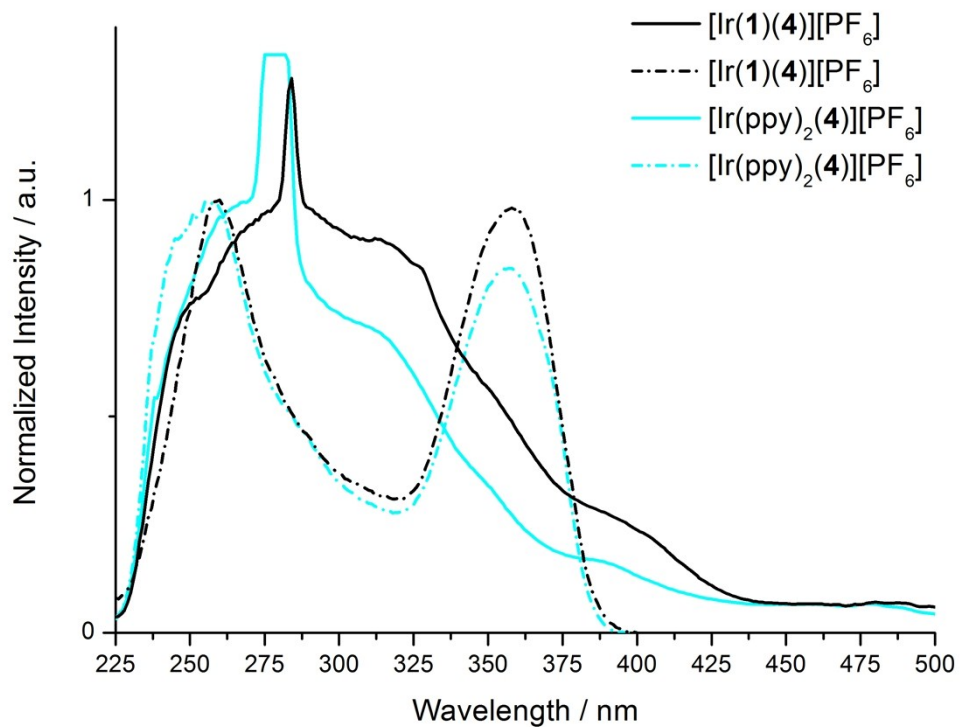
Andreas Bünzli,<sup>a</sup> Antonio Pertegás,<sup>b</sup> Cristina Momblona,<sup>b</sup> José M. Junquera-Hernández,<sup>b</sup> Edwin C. Constable,<sup>a</sup> Henk J. Bolink,<sup>b</sup> Enrique Ortí\*<sup>b</sup> and Catherine E. Housecroft\*<sup>a</sup>

<sup>a</sup> *Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland; email: catherine.housecroft@unibas.ch*

<sup>b</sup> *Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán 2, Paterna, E-46980, Spain; e-mail: enrique.orti@uv.es*

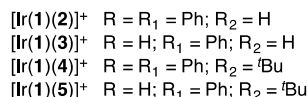
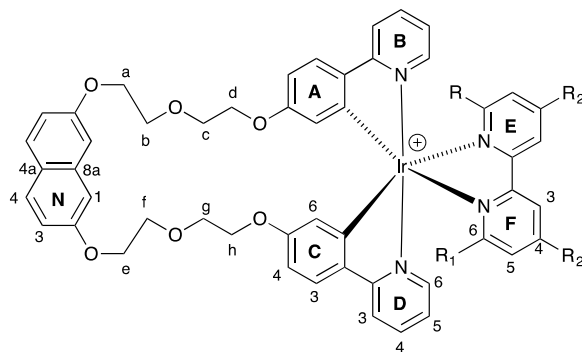


**Fig. S1.** Normalized photoluminescence spectra of complexes  $[\text{Ir}(\mathbf{1})(N^N)](\text{PF}_6)$  with  $N^N = 2-5$  in amorphous thin film upon excitation at 320 nm. The complex is mixed with the ionic liquid 1-butyl-3-methylimidazolium hexafluoridophosphate  $[\text{Bmim}][\text{PF}_6]$  in a ratio 4:1 (complex:ionic liquid).



**Fig. S2.** Excitation spectra measured for  $1.00 \times 10^{-5}$  M  $\text{CH}_2\text{Cl}_2$  solutions containing  $[\text{Ir}(\mathbf{1})(\mathbf{4})][\text{PF}_6]$  or  $[\text{Ir}(\text{ppy})_2(\mathbf{4})][\text{PF}_6]$  with fixed emission wavelengths of 564 and 558 nm (solid lines) or of 420 nm (dashed lines), respectively. (The spikes at 282 and 279 nm are the upper harmonics of the fixed emissions at 564 and 558 nm.)

**Table S1** Selected geometrical parameters computed at the B3LYP-D3/(6-31G\*\*+LANL2DZ) level for the  $S_0$  and  $T_1$  states of complexes  $[\text{Ir}(\mathbf{1})(\text{N}^{\wedge}\text{N})]^+$  ( $\text{N}^{\wedge}\text{N} = \mathbf{2-5}$ ) and  $[\text{Ir}(\text{ppy})_2(\mathbf{4})]^+$  in  $\text{CH}_2\text{Cl}_2$  solution without imposing any symmetry restriction.  $T_1$  was calculated using the spin-unrestricted UB3LYP-D3 approach.

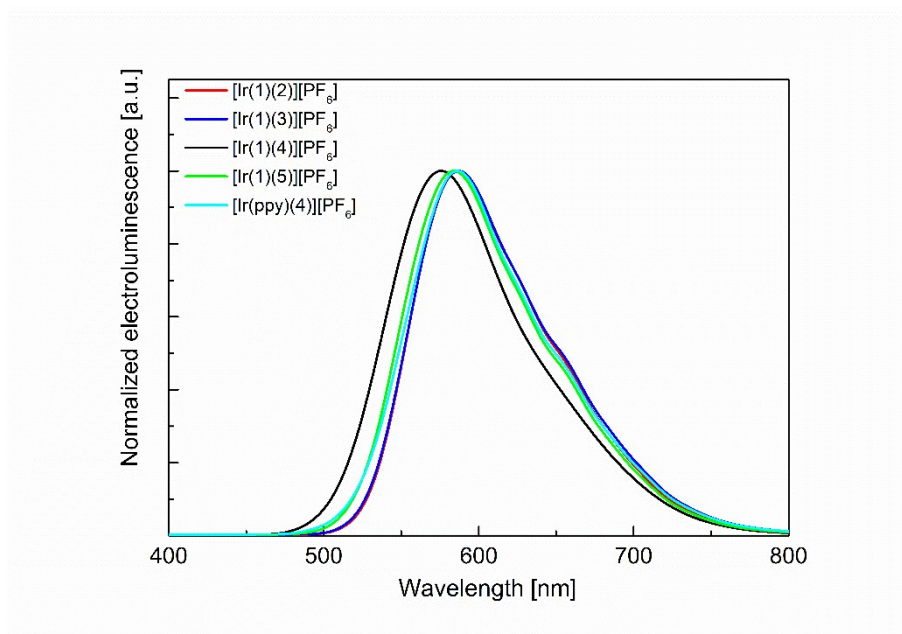


	$[\text{Ir}(\mathbf{1})(\mathbf{2})]^+$		$[\text{Ir}(\mathbf{1})(\mathbf{3})]^+$		$[\text{Ir}(\mathbf{1})(\mathbf{4})]^+$		$[\text{Ir}(\mathbf{1})(\mathbf{5})]^+$		$[\text{Ir}(\text{ppy})_2(\mathbf{4})]^+$	
	$S_0$	$T_1$	$S_0$	$T_1$	$S_0$	$T_1$	$S_0$	$T_1$	$S_0$	$T_1$
<b>Distances (Å)</b>										
Ir – N(E)	2.26	2.19	2.17	2.17	2.26	2.20	2.17	2.17	2.26	2.20
Ir – N(F)	2.30	2.26	2.27	2.22	2.31	2.26	2.27	2.21	2.30	2.26
Ir – N(B)	2.06	2.05	2.06	2.06	2.06	2.06	2.06	2.06	2.05	2.06
Ir – N(D)	2.07	2.08	2.07	2.07	2.07	2.08	2.07	2.06	2.07	2.08
Ir – C <sub>i</sub> (A)	2.00	1.98	2.00	2.01	2.00	1.98	2.00	2.01	2.01	1.98
Ir – C <sub>i</sub> (C)	2.01	2.00	2.02	1.98	2.01	2.00	2.02	1.98	2.01	2.00
Ir – Naphtyl <sup>a</sup>	10.77	10.56	10.61	10.55	10.78	10.59	10.62	10.52	--	--
Ctr(A) – Ctr(G) <sup>b</sup>	3.43	3.53	--	--	3.44	3.42	--	--	3.43	3.46
Ctr(C) – Ctr(G <sub>1</sub> )	3.51	3.40	3.42	3.37	3.52	3.52	3.40	3.37	3.57	3.57
<b>Angles (°)</b>										
N(E) – Ir – N(F)	74.54	75.20	75.15	76.32	74.43	75.14	75.08	76.28	74.33	74.71
N(B) – Ir – N(E)	88.15	92.04	88.12	87.36	87.74	91.09	87.61	87.29	87.04	91.01
N(D) – Ir – N(F)	82.14	83.32	84.92	84.90	81.40	80.97	84.25	84.92	81.22	80.91
N(B) – Ir – C <sub>1</sub> (A)	80.34	80.80	80.46	80.75	80.40	80.71	80.47	80.79	80.36	80.63
N(D) – Ir – C <sub>1</sub> (C)	80.28	81.20	80.19	81.22	80.31	81.10	80.20	81.24	80.12	81.00
<b>Dihedral Angles (°)<sup>c</sup></b>										
E – F	32.79	2.45	21.33	13.18	38.27	17.49	24.88	14.87	37.11	14.21
C – G <sub>1</sub>	8.66	7.27	3.94	5.73	10.01	7.29	4.00	5.22	9.73	6.79
A – G	4.48	4.47	--	--	4.23	4.38	--	--	6.35	6.44

<sup>a</sup> Distance from the Ir atom to the mass centre of the naphthyl group. <sup>b</sup> Ctr denotes the centroid of the ring indicated within parentheses following the nomenclature used in the figure (G and G<sub>1</sub> are the phenyl rings attached as R and R<sub>1</sub>). <sup>c</sup> The values reported correspond to the angle formed by the average planes of the rings indicated.

**Table S2** Lowest triplet excited states ( $T_n$ ) calculated at the TD-DFT B3LYP-D3/(6-31G\*\*+LANL2DZ) level for complexes  $[\text{Ir}(\mathbf{1})(\text{N}^{\wedge}\text{N})]^+$  ( $\text{N}^{\wedge}\text{N} = \mathbf{2-5}$ ) and  $[\text{Ir}(\text{ppy})_2(\mathbf{4})]^+$  in  $\text{CH}_2\text{Cl}_2$  solution. Vertical excitation energies ( $E$ ), dominant monoexcitations with contributions (within parentheses) greater than 20%, nature of the electronic transition and description of the excited state are summarized. H and L denote HOMO and LUMO, respectively.

State	$E$ (eV)	Monoexcitations	Nature	Description
$[\text{Ir}(\mathbf{1})(\mathbf{2})]^+$				
$T_1$	2.48	H $\rightarrow$ L (84)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_2$	2.68	H $\rightarrow$ L+1 (34)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_3$	2.71	H $\rightarrow$ L+3 (20)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{C}^{\wedge}\text{N}}^* + \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{LC}(\text{C}^{\wedge}\text{N})/{}^3\text{MLCT}/{}^3\text{LLCT}$
$T_4$	2.85	H-1 $\rightarrow$ L+7 (87)	$\pi_{\text{Naph}} \rightarrow \pi_{\text{Naph}}^*$	${}^3\text{LC}(\text{Naph})$
$[\text{Ir}(\mathbf{1})(\mathbf{3})]^+$				
$T_1$	2.43	H $\rightarrow$ L (86)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_2$	2.69	H $\rightarrow$ L+1 (46)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_3$	2.73	H-2 $\rightarrow$ L+1 (32)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{C}^{\wedge}\text{N}}^*$	${}^3\text{LC}(\text{C}^{\wedge}\text{N})/{}^3\text{MLCT}$
$T_4$	2.82	H-2 $\rightarrow$ L (79)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_5$	2.86	H-1 $\rightarrow$ L+7 (87)	$\pi_{\text{Naph}} \rightarrow \pi_{\text{Naph}}^*$	${}^3\text{LC}(\text{Naph})$
$[\text{Ir}(\mathbf{1})(\mathbf{4})]^+$				
$T_1$	2.55	H $\rightarrow$ L (68)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_2$	2.69	H-2 $\rightarrow$ L+1 (24)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_3$	2.74	H $\rightarrow$ L+2 (21)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{C}^{\wedge}\text{N}}^* + \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{LC}(\text{C}^{\wedge}\text{N})/{}^3\text{MLCT}/{}^3\text{LLCT}$
$T_4$	2.85	H-1 $\rightarrow$ L+7 (87)	$\pi_{\text{Naph}} \rightarrow \pi_{\text{Naph}}^*$	${}^3\text{LC}(\text{Naph})$
$[\text{Ir}(\mathbf{1})(\mathbf{5})]^+$				
$T_1$	2.53	H $\rightarrow$ L (83)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_2$	2.69	H $\rightarrow$ L+1 (39)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_3$	2.73	H-2 $\rightarrow$ L+1 (32)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{C}^{\wedge}\text{N}}^*$	${}^3\text{LC}(\text{C}^{\wedge}\text{N})/{}^3\text{MLCT}$
$T_4$	2.86	H-1 $\rightarrow$ L+7 (87)	$\pi_{\text{Naph}} \rightarrow \pi_{\text{Naph}}^*$	${}^3\text{LC}(\text{Naph})$
$[\text{Ir}(\text{ppy})_2(\mathbf{4})]^+$				
$T_1$	2.56	H $\rightarrow$ L (67)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_2$	2.74	H $\rightarrow$ L+2 (26)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
$T_3$	2.80	H $\rightarrow$ L (25)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{C}^{\wedge}\text{N}}^*$	${}^3\text{MLCT}/{}^3\text{LLCT}$
		H $\rightarrow$ L+1 (24)	$d_{\pi}(\text{Ir}) + \pi_{\text{C}^{\wedge}\text{N}} \rightarrow \pi_{\text{N}^{\wedge}\text{N}}^*$	${}^3\text{LC}(\text{C}^{\wedge}\text{N})/{}^3\text{MLCT}$



**Fig. S3.** Normalized electroluminescence spectra recorded for complexes  $[\text{Ir}(\mathbf{1})(N^N)]$  with  $N^N = 2-5$  and  $[\text{Ir}(\text{ppy})(\mathbf{4})][\text{PF}_6]$  when incorporated in ITO/PEDOT:PSS/Active layer/Al LECs operated under a pulsed current driving (average current density  $25 \text{ A m}^{-2}$ , 1000 Hz, 50% duty cycle). Active layer = Ir-iTMC:[Bmim][PF<sub>6</sub>] 4:1 molar ratio.