Electronic Supporting Information

Regioisomerism in cationic sulfonyl-substituted $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ complexes: influence on photophysical properties and LEC performance

Cathrin D. Ertl,[a] Lidón Gil-Escrig,[b] Jesús Cerdá,[b] Antonio Pertegás,[b] Henk J. Bolink,[b] José M. Junquera-Hernández,[b] Alessandro Prescimone,[a] Markus Neuburger,[a] Edwin C. Constable,[a] Enrique Ortí*[b] and Catherine E. Housecroft*[a]

[a] *Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland.*
[b] *Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán 2, Paterna, E-46980, Spain.*

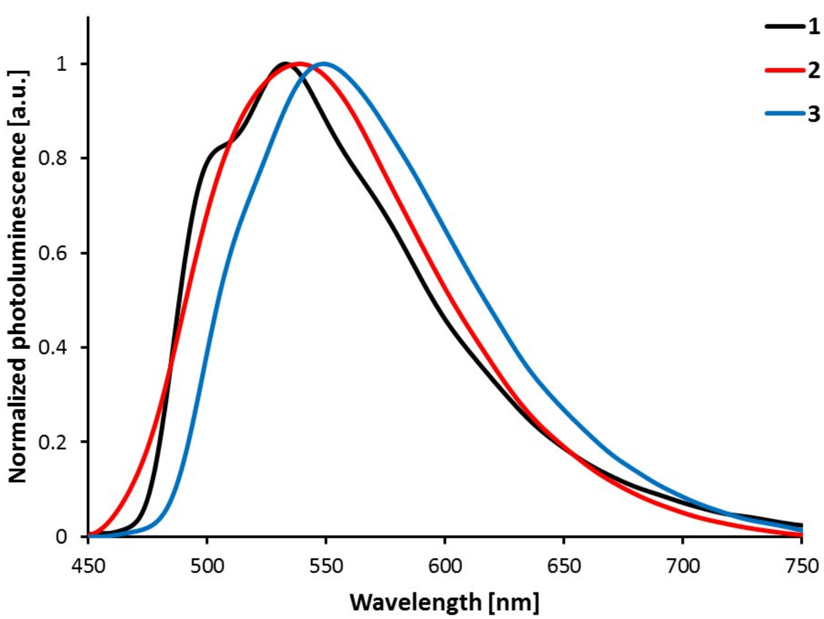

Fig. S1 Normalized photoluminescence spectra of complexes $[Ir(C^\wedge N)_2(bpy)][PF_6]$ with C^N = [**1**]⁻ to [**3**]⁻ in the thin film configuration used in LEC devices. The complex is mixed with the ionic liquid $[Bmim][PF_6]$ in a complex:IL 4:1 molar ratio.

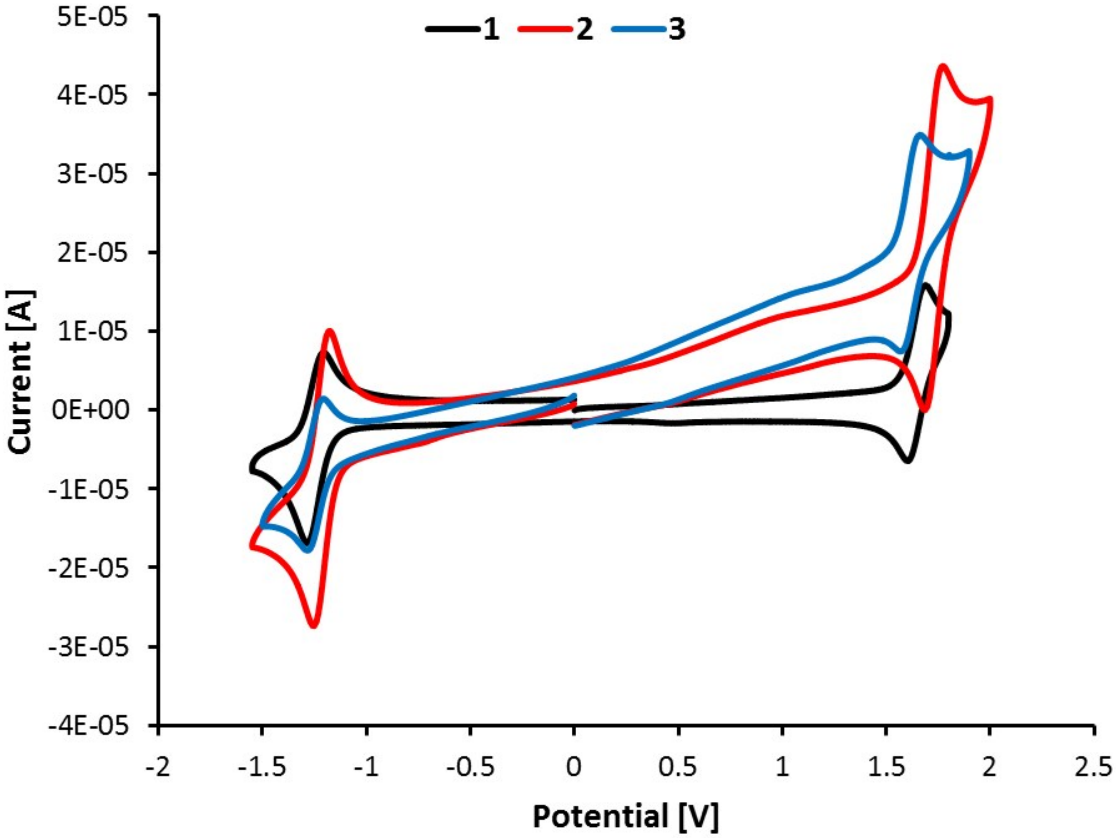

Fig. S2. Cyclic voltammograms showing the first oxidation and reduction processes of $[Ir(C^\wedge N)_2(bpy)][PF_6]$ (C^N = [**1**]$^-$, [**2**]$^-$ or [**3**]$^-$) in MeCN solution referenced to Fc/Fc^+ with 0.1 M $[^nBu_4][PF_6]$ as supporting electrolyte and a scan rate of 0.1 V s^{-1}.

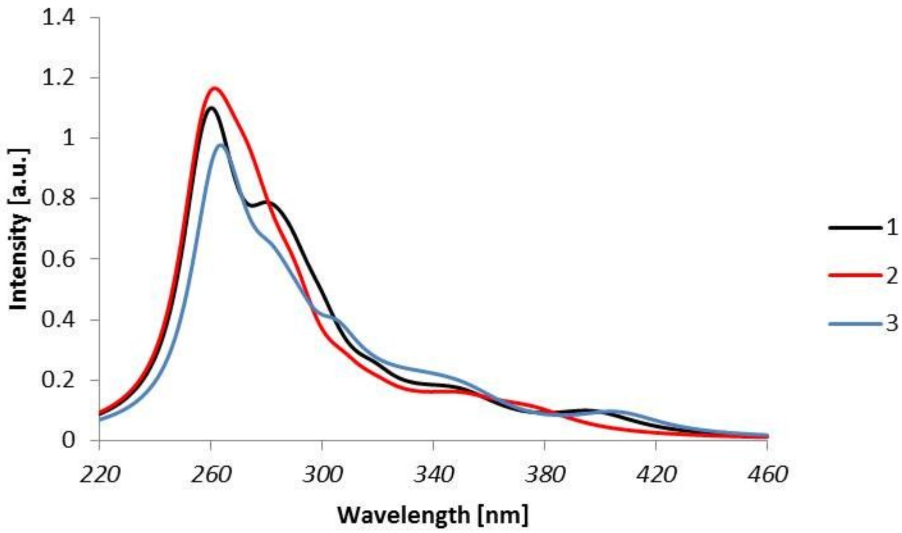

Fig. S3 Theoretical simulation of the absorption spectrum of complexes [Ir(C^N)$_2$(bpy)][PF$_6$] with C^N = [**1**]$^-$ to [**3**]$^-$ obtained from TD-DFT/B3LYP/(6-31G** + LANL2DZ) calculations of the 40 lowest-energy singlet excited states. The spectra have been obtained as convoluted sums of Lorentzian curves. Each curve is centered on the wavelength value calculated for a singlet excited state, and its area is proportional to the oscillator strength.

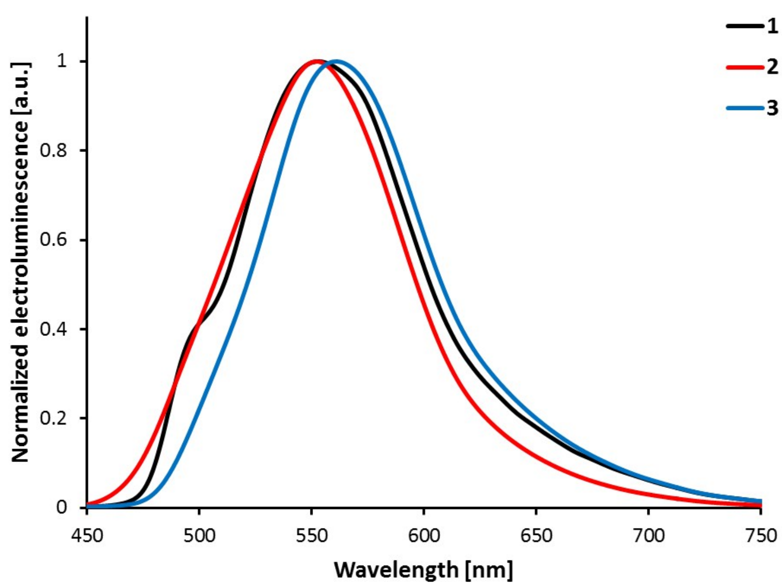

Fig. S4 Normalized electroluminescence spectra of ITO/PEDOT:PSS/active layer/Al LEC devices measured by applying a block-wave pulsed current of 100 A m^{-2} at a frequency of 1 kHz and duty cycles of 50%. Active layer: [Ir(C^N)$_2$(bpy)][PF$_6$] (C^N = [**1**]$^-$ to [**3**]$^-$) : [Bmim][PF$_6$] 4:1 molar ratio.

Table S1 Lowest singlet excited states calculated at the TD-DFT B3LYP/(6-31G**+LANL2DZ) level for complexes $[Ir(\mathbf{1})_2(bpy)]^+$, $[Ir(\mathbf{2})_2(bpy)]^+$ and $[Ir(\mathbf{3})_2(bpy)]^+$ in acetonitrile. Vertical excitation energies (*E*), oscillator strengths (*f*), dominant monoexcitations with contributions (within parentheses) greater than 20% and description of the excited state. H and L denote HOMO and LUMO, respectively.

Complex	State	*E* (eV/nm)	*f*	Monoexcitations	Description
$[Ir(\mathbf{1})_2(bpy)]^+$	S_1	2.81/441	0.000	H → L (98)	^{1}MLCT/LLCT
	S_2	3.12/397	0.067	H → L+1 (97)	^{1}LC
	S_5	3.55/349	0.097	H-1 → L (50)	^{1}MLCT/LLCT
$[Ir(\mathbf{2})_2(bpy)]^+$	S_1	2.89/429	0.000	H → L (99)	^{1}MLCT/LLCT
	S_2	3.30/375	0.058	H → L+1 (96)	^{1}LC
	S_5	3.55/350	0.084	H-1 → L (51)	^{1}MLCT/LLCT
$[Ir(\mathbf{3})_2(bpy)]^+$	S_1	2.79/445	0.000	H → L (98)	^{1}MLCT/LLCT
	S_2	3.05/406	0.067	H → L+1 (97)	^{1}LC
	S_5	3.53/351	0.084	H-1 → L (50)	^{1}MLCT/LLCT