Simple Design to Achieve Red-to-Near-infrared Emissive

Cationic Ir(III) Emitters and their use in Light Emitting

Electrochemical Cells

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Table of Contents:

Experimental section	
NMR spectra of complexes	S10-S11
X-ray Crystallographic section	
Electrochemistry	
DFT calculations and UV-vis study	
Steady-state emission profiles and spin densities	S17
XYZ Coordinates of DFT optimized structures	
Photoluminescence in thin film	
Device characteristics	
Notes and References	

Experimental Section

General Synthetic Procedures. Commercial chemicals were used as supplied. All reactions were performed using standard Schlenk techniques under an inert (N2) atmosphere. Purification and handling of all compounds were carried out under air. All products were stored in the dark. Freshly distilled anhydrous toluene was obtained from a Pure SolvTM solvent purification system (Innovative Technologies). Chromatography was performed on columns with an i.d. of 25–30 mm on silica gel (Geduran[®] Silicagel 60, 40–63 µm; Merck). The progress of reactions and the elution of products were followed by TLC (silica gel on aluminum sheets, SiliaPlate[™] TLC Plates, Silicycle, 250 µm with indicator F-254). Compounds were visualised under UV light. ¹H and ¹³C NMR spectra were recorded with Bruker AVANCE II spectrometer (500 MHz for ¹H; 125 MHz for ¹³C). The following abbreviations have been used for multiplicity assignments: "s" for singlet, "d" for doublet, "t" for triplet, "p" for pentet, "m" for multiplet, and "br" for broad. ¹H NMR spectra were referenced to the solvent peak. Melting points (Mp) were recorded using open-end capillaries on an Electrothermal melting point apparatus IA9200 and are uncorrected. The heating rate was 0.5 or 1.0 °C/min. Highresolution mass spectra were recorded by EPSRC National Mass Spectrometry Service Centre, Swansea University. Elemental analyses were performed by Mr. Stephen Boyer, London Metropolitan University.

Photophysical measurements. All samples were prepared in HPLC grade acetonitrile (MeCN) with varying concentrations on the order of μ M. Absorption spectra were recorded at RT using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least-squares fit of values obtained from at least five independent solutions at varying concentrations with absorbance ranging from 6.88×10^{-1} to $3.19 \times 10^2 \mu$ M.

The sample solutions for the emission spectra were prepared in N₂-degassed (20 minutes) HPLC grade MeCN using an in-house designed quartz cuvette. Steady-state and time-resolved emission spectra were recorded at room temperature using a Gilden fluoroSENS fluorimeter. The samples were excited at the absorption maxima of the dominant low-energy ¹MLCT/³MLCT band as indicated in Table S4. Excited state lifetimes were measured by time correlated single photon counting (TCSPC) with an Edinburgh Instruments FLS980 fluorimeter using a pulsed diode laser (exciting at 378 nm) and PL emission was detected at the corresponding steady-state emission maximum for each complex. The PL decays were fitted to a single exponential decay function. Emission quantum yields were determined using the optically dilute method.¹ A stock solution with absorbance of ca. 1.1 was prepared and then four dilutions were prepared with dilution factors of 43.2, 21, 13.7 and 10 to obtain solutions with absorbances of ca. 0.025 0.050, 0.075 and 0.1, respectively. The Beer-Lambert law was found to be linear at the concentrations of the solutions. The emission spectra were then measured after the solutions were rigorously degassed with solvent-saturated N₂ gas for 20 minutes prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified through linear regression analysis and additional measurements were acquired until the Pearson regression factor (R^2) for the linear fit of the data set surpassed 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the slope value. The equation $\Phi_s = \Phi_r (A_r/A_s) (I_s/I_r) (n_s/n_r)^2$ was used to calculate the relative quantum yield of each of the sample, where Φ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. An aerated solution of [Ru(bpy)₃]Cl₂ in water ($\Phi_r = 0.04$) was used as the external reference.²

The samples for thin-film photoluminescence (PL) measurements were done with the same composition and thickness than the emissive layer of LEECs. Each complex was mixed with the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] in a 4-to-1 molar ratio (iTMC:IL) and deposited onto a quartz plate. A Hamamatsu absolute quantum yield C9920 instrument was used for the steady-state emission spectra and determination of photoluminescence quantum yields of the doped thin-films. A Hamamatsu Compact fluorescence lifetime spectrometer C11367 instrument was used to determine the excited state lifetimes of the doped thin-films.

Electrochemistry measurements. Cyclic voltammetry (CV) measurements were performed in N₂purged HPLC grade acetonitrile at room temperature with an electrochemical analyzer potentiostat model 620E from CH Instruments interfaced to a PC at a sweep rate of 100 mV/s. Differential pulse voltammetry (DPV) was conducted with an increment potential of 0.004 V and a pulse amplitude, width, and period of 50 mV, 0.05, and 0.5 s, respectively. Solutions for CV and DPV were prepared in MeCN and degassed with MeCN-saturated N₂ bubbling for about 10 min prior to scanning. Tetra(*n*-butyl)ammonium hexafluorophosphate (TBAPF₆; *ca.* 0.1 M in MeCN) was used as the supporting electrolyte. A silver wire was used as the pseudoreference electrode; a glassy-carbon electrode was used for the working electrode and a Pt wire was used as the counter electrode. The redox potentials are reported relative to a standard calomel electrode (SCE) electrode with a ferrocenium/ferrocene (Fc^+/Fc) redox couple as an internal reference (0.38 V vs SCE).³

Experimental uncertainties are as follows: absorption maxima, ± 2 nm; molar absorption coefficient, 10%; redox potentials, ± 10 mV; emission maxima, ± 3 nm; emission lifetimes, $\pm 10\%$; luminescence quantum yields, $\pm 10\%$.

Device preparation. LEECs were prepared on top of a patterned indium tin oxide (ITO, 15 Ω square⁻¹) coated glass substrate (www.naranjosubstrates.com) previously cleaned as follows: a)

sonication with soap, b) deionized water, c) isopropanol, and d) UV-O₃ lamp for 20 min. The thickness of the films was determined with an Ambios XP-1 profilometer. Prior to the deposition of the emitting layer, a 80 nm thick film of poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (CLEVIOS[™] P VP AI 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was coated in order to avoid the formation of pinholes and to increase the reproducibility of the cells. The emitting layer (100 nm) was prepared by spin-coating of a dichloromethane solution consisting of the iTMC with the addition of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF₆] (> 98.5%, Sigma-Aldrich) in a 4:1 molar ratio (iTMC:IL). For obtaining a good layer morphology, after adding the dichloromethane solution the substrate was covered during spinning. This fact slowed down the evaporation of the solvent and lead to more homogeneous and better-quality film. The devices were then transferred to an inert atmosphere glovebox (< 0.1 ppm O₂ and H₂O, MBraun). Finally, a layer (70 nm) of aluminium (the top electrode) was thermally evaporated onto the devices using an Edwards Auto500 evaporator integrated in the inert atmosphere glovebox. The area of the device was 6.5 mm². The devices were not encapsulated and were characterized inside the glovebox at room temperature.

Device characterization. The device lifetime was measured by applying a pulsed current and monitoring the voltage *versus* time with a Botest OLT OLED Lifetime-Test System. The radiance was monitored using an integrating sphere (UDT Instruments, model 2525LE) coupled to a Radiometric Sensor (UDT Instruments, model 247) and an optometer (UDT Instruments, model S370). The electroluminescent (EL) spectra were measured using an Avantes AvaSpec-2048 Fiber Optic Spectrometer during device lifetime measurement. The peak current density of the pulse was 800 and 1600 A m⁻² and the average current density is determined by multiplying the peak current density by the time-on time and dividing by the total cycle time 50%.

2,2'-Bithiazole, L1.



2-Bromothiazole (2.00 g, 12.20 mmol, 1 equiv.), *N,N'*-diisopropylethylamine (DIPEA) (2.13 mL, 12.20 mmol, 1 equiv.), *n*-Bu₄NBr (1.97 g, 6.10 mmol, 0.50 equiv.) and Pd(OAc)₂ (0.14 g, 0.61 mmol, 0.05 equiv., 0.06 mol%) were dissolved in nitrogen-degassed toluene (35 mL). The mixture was heated to reflux for 20 h, after which time distilled water (50 mL) was added to the dark-brown solution before cooling down the solution to room temperature. The mixture was stirred at room temperature and dichloromethane (100 mL) was added. The organic layer was carefully separated and this procedure was repeated one more time with additional dichloromethane (50 mL). The organic layers were combined and evaporated to dryness to give dark brown oil. To this oil was added diethylether (200 mL) and the mixture was sonicated for 30 min. The ether solution was carefully decanted out and evaporated to dryness to afford the product as dark-orange microcrystalline solid. **Yield**: 0.85 g, 41%. **Mp:** 96-99 °C. ¹**H NMR (500 MHz, CDCl₃) \delta (ppm):** 7.45 (d, *J* = 3.21 Hz, 1 H), 7.90 (d, *J* = 3.21 Hz, 1 H). ¹³**C NMR (126 MHz, CD₃CN) \delta (ppm):** 161.79, 144.05, 121.12. Characterisation data match that reported in literature.⁴

2,2'-bibenzo[d]thiazole, L2.

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2-Bromobenzthiazole (2.00 g, 9.34 mmol, 1 equiv.), *N*,*N*'-diisopropylethylamine (DIPEA) (1.63 mL, 9.34 mmol, 1 equiv.), *n*-Bu₄NI (1.73 g, 4.67 mmol, 0.50 equiv.) and Pd(OAc)₂ (0.21 g, 0.93 mmol, 0.1 equiv., 0.09 mol%) were dissolved in nitrogen-degassed toluene (35 mL). The mixture was heated to reflux for 20 h, after which time distilled water (50 mL) was added to the dark-brown solution before cooling down the solution to room temperature. The mixture was stirred at room temperature and dichloromethane (100 mL) was added. The organic layer was carefully separated and this procedure was repeated one more time with additional dichloromethane (50 mL). The organic layers were combined and evaporated to dryness to give dark brown oil. To this oil was added diethylether (200 mL) and the mixture was sonicated for 30 min. The ether solution was carefully decanted out and evaporated to dryness to afford the product as dark-orange microcrystalline solid. **Yield**: 1.27 g, 51%. **Mp:** 238-241 °C (dec.). ¹**H NMR (500 MHz, CDCl₃) \delta (ppm): 8.17 (d,** *J* **= 8.27 Hz, 1H), 7.99**

(d, J = 8.05 Hz, 1H), 7.57 (t, J = 7.72 Hz, 1H), 7.50 (t, J = 7.67 Hz, 1H). ¹³C NMR (126 MHz, CD₃CN) δ (ppm): 161.68, 153.69, 135.94, 127.00, 126.79, 124.23, 122.20. Characterisation data match that reported in literature.⁵

Bis(2-phenylpyridinato- C^2 , N')(2,2'-bithiazole-N', N')iridium(III) hexafluorophosphate, 1.



A 100 mL round-bottomed flask was charged with tetrakis[2-phenylpyridinato- $N, C^{2'}$]-bis(μ chloro)diiridium(III) (0.100 g, 0.092 mmol, 1 equiv.) and 2,2'-bithiazole (0.033 g, 0.193 mmol, 2.1 equiv.). An aliquot of a mixture of dichloromethane and methanol (40 mL, 1:1, v/v) was added to the flask and the solution was degassed with nitrogen. The solution was heated to reflux under a nitrogen atmosphere for 20 h. The solution was cooled down to room temperature and the solvent was evaporated to dryness under reduced pressure to afford a red solid. Purification by flash column chromatography (silica, dichloromethane/methanol, 95:5, v/v) and subsequent anion metathesis by addition of an aliquot of saturated aqueous solution of KPF₆ afforded the product as an orange-yellow solid. The Crystals of suitable X-ray quality were grown by slow diffusion of diethylether into a concentrated solution of the title compound in dichloromethane. Yield: 0.138 g, 91%. Mp: 345-348 ^oC (dec.) R_f: 0.48 (dichloromethane/methanol, 95:5, v/v on silica). ¹H NMR (500 MHz, CD₃CN) δ (ppm): 6.26 - 6.32 (m, 1 H), 6.90 (td, J = 7.48, 1.28 Hz, 1 H), 7.03 (ddd, J = 7.85, 7.21, 1.18 Hz, 1 H), 7.08 (ddd, J = 7.37, 5.88, 1.28 Hz, 1 H), 7.23 (d, J = 3.42 Hz, 1 H), 7.60 (dd, J = 5.77, 0.64 Hz, 1 H), 7.78 (dd, J = 7.80, 1.18 Hz, 1 H), 7.84 - 7.89 (m, 1 H) 7.92 (d, J = 3.21 Hz, 1 H), 8.04 (dd, J =8.12, 0.85 Hz, 1 H). ¹³C NMR (126 MHz, CD₃CN) δ (ppm): 168.27, 162.71, 150.91, 147.63, 145.24, 142.75, 139.54, 132.53, 130.98, 128.60, 125.61, 124.56, 123.56, 120.56. HR NSI⁺ MS: [M- $\mathbf{PF_6}^{\dagger}$ Calculated: (C₂₈H₂₀N₄S₂Ir) 669.0758; Found: 669.0744. Anal. Calcd. for C₂₈H₂₀N₄F₆PS₂Ir: C, 41.33; H, 2.48; N, 6.88; Found: C, 41.95; H, 2.72; N, 6.82.

Bis(2-phenylpyridinato- C^2 , N')(2,2'-bibenzo[d]thiazole-N', N')iridium(III) hexafluorophosphate, 2.



A 100 mL round-bottomed flask was charged with tetrakis[2-phenylpyridinato- $N, C^{2'}$]-bis(μ chloro)diiridium(III) (0.100 g, 0.092 mmol, 1 equiv.) and 2,2'-bibenzo[d]thiazole (0.057 g, 0.211 mmol, 2.3 equiv.). An aliquot of a mixture of dichloromethane and methanol (40 mL, 1:1, v/v) was added to the flask and the solution was degassed with nitrogen. The solution was heated to reflux under a nitrogen atmosphere for 20 h. The solution was cooled down to room temperature and the solvent was evaporated to dryness under reduced pressure to afford a brownish-red solid. Purification by flash column chromatography (silica, dichloromethane/methanol, 95:5, v/v) and subsequent anion metathesis by addition of an aliquot of aqueous saturated solution of KPF₆ afforded the product as a red solid. The Crystals of suitable X-ray quality were grown by slow diffusion of diethylether into a concentrated solution of the title compound in dichloromethane. Yield: 0.160 g, 95%. Mp: 388-390 °C (dec.) R_f: 0.45 (dichloromethane/methanol, 95:5, v/v on silica). ¹H NMR (500 MHz, CD₃CN) δ (ppm): 8.20 (dt, J = 8.3, 1.0 Hz, 1H), 8.03 (dt, J = 8.2, 1.1 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.72 (ddd, J= 5.8, 1.5, 0.8 Hz, 1H), 7.57 (ddd, J = 8.3, 7.2, 1.1 Hz, 1H), 7.24 (ddd, J = 8.5, 7.2, 1.2 Hz, 1H), 7.15 (td, J = 7.6, 1.2 Hz, 1H), 6.98 (dtd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 7.4, 5.5, 1.4 Hz, 2H), 6.83 (dt, J = 8.6, 0.9 Hz, 1H), 6.32 (dd, J = 8.6, 0.9 Hz, 1H), 6.34 (dd, Hz, 1H), 6.3= 7.7, 1.2 Hz, 1H). ¹³C NMR (126 MHz, CD₃CN) δ (ppm): 167.90, 164.67, 151.64, 151.38, 145.94, 145.63, 139.71, 136.86, 132.67, 131.17, 129.80, 129.72, 125.88, 124.83, 124.79, 124.14, 123.27, 120.70. HR NSI⁺ MS: [M-PF₆]⁺ Calculated: (C₃₆H₂₄N₄S₂Ir) 769.1065; Found: 769.1061. Anal. **Calcd.** for C₃₆H₂₄N₄F₆PS₂Ir: C, 47.31; H, 2.65; N, 6.13; Found: C, 47.17; H, 2.84; N, 6.17.



Fig. S1: ¹H NMR spectrum of complex 1 in CD₃CN at 500 MHz at r.t. (peak at ~ 5.3 ppm corresponds to residual DCM in CD₃CN).



Fig. S2: ¹³C NMR spectrum of complex 1 in CD₃CN at 500 MHz at r.t. (peak at ~ 30 ppm corresponds to residual DCM in CD₃CN).



Fig. S3: ¹H NMR spectrum of complex 2 in CD₃CN at 500 MHz at r.t.



Fig. S4: ¹³C NMR spectrum of complex 2 in CD₃CN at 500 MHz at r.t.

X-Ray Crystallography

Single crystals were grown by vapour diffusion of diethyl ether into either concentrated CH_2Cl_2 solution (1) or concentrated MeCN solution (2). Data were collected at 173 K (1) or 93 K (2) on a Rigaku FR-X Ultrahigh brilliance Microfocus RA generator/confocal optics with Rigaku XtaLAB P200 system, using Mo K α radiation ($\lambda = 0.71075$ Å). Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects, and a multiscan absorption correction was applied by using CrystalClear.⁶ Structures were solved by Patterson methods (PATTY)⁷ and refined by full-matrix least-squares against F² (SHELXL-2013).⁸ Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model. All calculations were performed using the CrystalStructure interface.⁹

compound	1	2
empirical formula	C ₂₈ H ₂₀ F ₆ IrN ₄ PS ₂	C ₃₈ H ₂₇ F ₆ IrN ₅ PS ₂
fw	813.80	954 97
cryst syst	orthorhombic	orthorhombic
lattice	Primitive	Primitive
space group	<i>Pbca (#61)</i>	Pca21 (#29)
a [Å]	10.8949(11)	24.377(3)
b [Å]	15.8728(15)	9.1545(10)
c [Å]	33.006(4)	15.859(2)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
vol $[Å]^3$	5707.8(10)	3539.1(7)
Ζ	8	4
ρ (calc) [Mg/m ³]	1.894	1.792
μ [cm ⁻¹]	49.599	40.154
F(000)	3152.00	1872.00
cryst	orange, chip	red, prism
cryst size [mm ³]	$0.06 \times 0.03 \times 0.01$	$0.20 \times 0.10 \times 0.10$
θ range	2.240 - 25.371°	2.377 – 25.315 °
reflns collected	64336	17647
indep reflns (R _{int})	5220 (0.0622)	6135 (0.0256)
max/min transm	0.952 / 0.875	0.669 / 0.517
data/restraints/params	5220 / 0 / 379	6135 / 1 / 479
GOF on F^2	1.097	0.841
final R indices	R1 = 0.0336,	R1 = 0.0185,
$[I > 2\sigma(I)]$	wR2 = 0.0571	wR2 = 0.0360
R indices	R1 = 0.0743,	R1 = 0.0200,
(all data)	wR2 = 0.0725	wR2 = 0.0362
largest diff. peak/hole	0.85 / -0.70	0.57 / -0.34
[e/Å ³]		

Table S1. Crystal Data and Structure Refinement

Table S2. Comparison of observed bond distances and angles in complexes 1 and 2 with values calculated for these complexes.^a

Compound	E	Bond Length (Å)		I	Angle (•)	
1		Obs.	Calc.		Obs.	Calc.
		(X-ray)	(DFT)		(X-ray)	(DFT)
	Ir1-N25 _{N^N}	2.148(6)	2.245	N1 _{C^N} -Ir1-C8 _{C^N}	80.6(2)	79.99
	$Ir1-N31_{N^{\wedge}N}$	2.149(6)	2.245	N13 _{C^N} -Ir1-C20 _{C^N}	80.7(2)	80.00
	Ir1-N1 _{C^N}	2.048(5)	2.090	N25 _{N^N} -Ir1-N31 _{N^N}	75.3(2)	74.19
	Ir1-N13 _{C^N}	2.046(5)	2.090			
	Ir1-C8 _{C^N}	2.007(6)	2.025			
	Ir1-C20 _{C^N}	2.003(7)	2.025			
2	Ir1-N1 _{C^N}	2.058(4)	2.089	N1 _{C^N} -Ir1-C8 _{C^N}	80.62(17)	80.01
	Ir1-N13 _{C^N}	2.049(4)	2.089	N13 _{C^N} -Ir1-C20 _{C^N}	80.45(17)	80.01
	Ir1-N25 _{N^N}	2.180(4)	2.285	N25 _{N^N} -Ir1-N35 _{N^N}	76.00(14)	74.09
	Ir1-N35 _{N^N}	2.195(4)	2.285			
	Ir1-C8 _{C^N}	2.009(4)	2.025			
	Ir1-C20 _{CON}	2.009(5)	2.025			

^aRestricted DFT geometry optimizations of $[1]^+$ and $[2]^+$ (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S]).



Fig. S5: Perspective views of complexes (a) 1 and (b) 2. Ellipsoids correspond to a 50% probability level. Anions, co-crystallised solvent molecule (in 2) and H-atoms have been omitted for clarity.

Electrochemistry

Table S3.	Redox potentials	of complexes 1	and 2 and the	e benchmark	complex	[Ir(ppy) ₂ (bpy)] ⁺ , R1
(where bp	y = 2,2'-bipyridine) in degassed M	eCN at 298 K	a			

Cmpd	$E_{1/2}^{O_{x}}(V)$	$E_{1/2}^{Red}(V)$	$\Delta \mathbf{E}_{redox}^{b}$	$E_{HOMO} (eV)^c$	$E_{LUMO} (eV)^{c}$	Δ E _{LUMO-HOMO}
			(V)			$(eV)^c$
1	1.24(110)	-1.15(74), -	2.38	-5.58	-2.76	2.82
		1.73(293),				
		-2.13(irr), -				
		2.29(213),				
		-2.83(irr)				
2	1.37(169)	-0.82(88), -	2.19	-5.80	-3.07	2.73
		1.46(89), -				
		2.37(103),				
		-2.66(171)				
$\mathbf{R1}^d$	1.27	-1.38	2.65	-5.56	-2.31	3.25

^{*a*}Potentials are in volts (V) *vs.* SCE for acetonitrile solutions, 0.1 M in $[n-Bu_4N]PF_6$, recorded at room temperature at a sweep rate of 100 mV/s using a glassy carbon electrode as a working electrode, a platinum wire as a counter electrode and a silver wire as a reference electrode. The difference between cathodic, E_{pc} , and anodic, E_{pa} , peak potentials, ΔE_p , (millivolts) is given in parentheses. ${}^{b}\Delta E_{redox}$ is the difference (V) between first oxidation and first reduction potentials. ^{*c*}DFT calculated energy in eV. ^{*d*}Redox potentials are from ref 10.



Fig. S6: Cyclic voltammogram (bold lines) and differential pulse voltammogram (dotted lines) of complexes 1 and 2 in degassed MeCN at r.t at a scan rate of 100 mV/s. Wave denoted with an asterix at 0.38 V corresponds to Fc/Fc^+ couple.

DFT Calculations:

All calculations were performed with the Gaussian09, revision D.01¹¹ suite of programs employing the DFT method, the Becke three-parameter hybrid functional,¹² and Lee-Yang-Parr's gradientcorrected correlation functional (B3LYP).¹³ Singlet and triplet ground state geometry optimizations and single point energy calculations for $[1]^+$, $[2]^+$ and $[R1]^+$ were carried out at the (R)B3LYP and (U)B3LYP levels, using their respective crystallographic structures as starting points. All elements except Iridium were assigned the 6-31G(d,p) basis set.¹⁴ The double- ζ quality SBKJC VDZ ECP basis set15 with an effective core potential was employed for the Ir(III)-ion. Vertical electronic excitations based on (R)B3LYP-optimized geometries were computed for $[1]^+$, $[2]^+$ and $[R1]^+$ using the TD-DFT formalism^{16a,b} in acetonitrile using conductor-like polarizable continuum model (CPCM).^{17a-c} Vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigenvalues. The electronic distribution and localization of the singlet excited states were visualized using the electron density difference maps (ED-DMs).¹⁸ Gausssum 2.2 and Chemissian v3.8¹⁹ were employed to visualize the absorption spectra (simulated with Gaussian distribution with a full-width at half maximum (fwhm) set to 3000 cm⁻¹) and to calculate the fractional contributions of various groups to each molecular orbital. All calculated structures and Kohn-Sham orbitals were visualized with ChemCraft.²⁰



Fig. S7: Calculated frontier MO energies of $[\mathbf{R1}]^+$, $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$, obtained from DFT [(rb3lyp/SBKJC-VDZ for Ir(III)) and (6-31g** for C,H,N,S)] with CPCM(MeCN) and 0.05 eV threshold of degeneracy. Kohn-Sham MOs of $[\mathbf{R1}]^+$, $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ are also shown (contours are isovalued at 0.03).

Table S4. UV-vis absorption data of complexes 1 and 2 (in degassed MeCN at room temperature) and benchmark complex R1.

Compound	$\lambda_{abs}/nm (\epsilon x 10^4 \text{ M}^{-1} \text{ cm}^{-1})$
1	252 (4.14), 265 (3.76), 303 (2.34), 318 (2.41), 333 (2.25), 377 (1.01), 466 (0.09), 500
	(0.07)
2	251 (3.92), 343 (1.98), 363 (2.64), 379 (2.82), 407 (1.03), 433 (0.50), 549 (0.06), 599
	(0.03)
R1 ^{<i>a</i>}	265 (4.17), 310 (1.29), 375 (0.60), 420 (0.26)
aa	

^aFrom ref. 10 in MeCN.



Fig. S8: Overlay of experimental UV-vis absorption spectra (curved lines) of complexes 1 and 2 with their predicted transitions (vertical bars) calculated by singlet TD-DFT at room temperature in MeCN.

Table S5. Selected transitions from TD-DFT calculations of $[1]^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm	$\lambda_{abs}/nm (\epsilon x 10^4 M^{-1} cm^{-1})$	f (TD-DFT)	Major transition(s)	character
	(TD-DFT)	[expt.]			
44	245	252 (4.14)	0.0707	H-12->L (72%)	L1(π) to L1(π *)
33	262	265 (3.76)	0.4271	H-6->L+1 (32%),	L1 (π) to ppy(π^*)
				H-1->L+4 (34%)	(minor) + ppy(π) to
					$ppy(\pi^*)$ (major)

18	291	303 (2.34)	0.1506	H-4->L+1 (67%)	ppy(π) to ppy(π^*) (major) + Ir($d\pi$) to ppy(π^*) (minor)
14	312	318 (2.41)	0.0762	H-1->L+2 (71%)	$ppy(\pi)$ to $ppy(\pi^*)$
9	327	333 (2.25)	0.3175	H-6->L (76%)	L1(π) to L1(π *)
4	396	377 (1.01)	0.0801	H-3->L (82%)	ppy(π) to L1(π^*) (major) + Ir($d\pi$) to L1(π^*) (minor)
2	434	466 (0.09)	0.0047	H-4->L (15%), H-2->L (81%)	ppy(π) to L1(π^*) (major) + Ir($d\pi$) to L1(π^*) (minor)
1	578	500 (0.07)	0.0001	H->L (99%)	$ppy(\pi) \text{ to } L1(\pi^*)$ $(major) + Ir(d\pi) \text{ to }$ $L1(\pi^*) \text{ (minor)}$

Table S6. Selected transitions from TD-DFT calculations of $[2]^+$ in the singlet ground state (B3LYP/SBKJC-VDZ[Ir]6-31G**[C,H,N,S], CPCM (MeCN)).

state	λ_{abs}/nm	$\lambda_{abs}/nm (\epsilon x 10^4 \text{ M}^{-1} \text{ cm}^{-1})$	f (TD-DFT)	Major transition(s)	character
	(TD-DFT)	[expt.]			
43	261	251 (3.92)	0.2385	H-7->L+1 (46%),	L2 (π) to ppy(π *)
				H-1->L+4 (36%)	(major) + ppy(π) to
					$ppy(\pi^*)$ (minor)
10	359	343 (1.98)	0.1065	H-7->L (92%)	$ppy(\pi)$ to $ppy(\pi^*)$
8	372	363 (2.64)	0.5763	H-6->L (91%)	L2(π) to L2(π *)
6	388	379 (2.82)	0.0191	H-5->L (97%)	ppy(π) to L2(π^*)
5	408	407 (1.03)	0.0201	H-4->L (96%)	$ppy(\pi)$ to $L2(\pi^*)$
4	426	433 (0.50)	0.0965	H-3->L (93%)	Ir($d\pi$) to L2 (π^*) (major)
					+ ppy(π) to L2 (π *)
					(minor)
2	466	549 (0.06)	0.0194	H-2->L (92%)	Ir($d\pi$) to L2 (π^*) (major)
					+ ppy(π) to L2(π *)
					(minor)
1	608	599 (0.03)	0.0001	H->L (99%)	Ir($d\pi$) to L2(π^*)
					$(minor) + ppy(\pi)$ to
					$L2(\pi^*)$ (major)



Fig. S9: Emission profiles of complexes 1 and 2 at r.t. in degassed MeCN ($\lambda_{exc} = 360$ nm). The shoulder at ~ 700 nm of complex 1 is due to instrumental artefact.



Fig. S10: Triplet spin density distributions of complexes **1** and **2**, obtained from DFT [(UB3LYP/SBKJC-VDZ for Ir(III)) and (6-31g** for C,H,N,S] with CPCM(MeCN). Contours are isovalued at 0.004.

Table S7. Optimized Atomic coordinates obtained from DFT calculations of $[1]^+$.

Center Numbe	At er N	omic Ato Number 7	отіс Гуре	Coordinate X Y	es (Angstroms) Z
1	77	0	0.163546	0.000108	0.000315
2	16	0	-4.162633	-1.069762	1.440592
3	16	0	-4.165051	1.055742	-1.443292
4	7	0	-1.626674	-0.770934	1.115220
5	7	0	-1.628373	0.765264	-1.115997
6	7	0	0.297520	-1.845705	-0.971581
7	7	0	0.289706	1.847220	0.971093
8	6	0	-2.796112	-0.424437	0.588496
9	6	0	1.587459	0.894539	-1.128493

10	6	0	1.899298	-2.223467	0.750219
11	6	0	-1.784511	1.565552	-2.220300
12	1	0	-0.905302	1.923656	-2.739621
13	6	0	-2.797057	0.414968	-0.590117
14	6	0	-0.275042	-3.431375	-2.677996
15	1	0	-0.861378	-3.664224	-3.559309
16	6	0	0.628688	-4.348185	-2.132226
17	1	0	0.763297	-5.325927	-2.583904
18	6	0	-0.291525	3.432305	2.675176
19	1	0	-0.880109	3.663716	3.555368
20	6	0	-3.082797	1.829765	-2.552554
21	1	0	-3.461813	2.425962	-3.370346
22	6	0	2.825245	2.992939	-1.471498
23	1	0	3.051807	4.013881	-1.178522
24	6	0	1.189076	-2.727209	-0.423416
25	6	0	2.833943	-2.983848	1.473758
26	1	0	3.064605	-4.003792	1.180495
27	6	0	1.357781	-3.992621	-1.006700
28	1	0	2.066894	-4.688005	-0.574525
29	6	0	3.471299	2.444476	-2.573209
30	1	0	4.193595	3.032842	-3.129785
31	6	0	1.892335	2.229642	-0.748793
32	6	0	1.178682	2.731624	0.423475
33	6	0	-0.408113	-2.194748	-2.066512
34	1	0	-1.086056	-1.443654	-2.453473
35	6	0	-1.781014	-1.571794	2.219364
36	1	0	-0.901031	-1.927059	2.739327
37	6	0	1.589155	-0.889706	1.130373
38	6	0	2.258629	0.366132	-2.240169
39	1	0	2.068091	-0.654297	-2.556810
40	6	0	1.341732	3.998183	1.005893
41	1	0	2.048860	4.695862	0.574167
42	6	0	3.476436	-2.433737	2.576742
43	1	0	4.200075	-3.019838	3.133964
44	6	0	2.256705	-0.359579	2.243391
45	1	0	2.061903	0.659952	2.560388
46	6	0	-3.078680	-1.840296	2.550611
47	1	0	-3.456340	-2.437803	3.368074
48	6	0	3.186174	1.129259	-2.953799
49	1	0	3.694308	0.693504	-3.809761
50	6	0	0.609588	4.352024	2.129973
51	1	0	0.739814	5.330677	2.580962
52	6	0	-0.418911	2.194621	2.064631
53	1	0	-1.094522	1.441284	2.451284
54	6	0	3.185986	-1.119823	2.957841
55	1	0	3.691290	-0.682844	3.814854

Center Number	Atomic Numb	er	Atomic Type	Coordinate X V	es (Angstroms)
1	77	0	-0.000039	-0.443672	0.000012
2	16	0	-1.690076	3.966726	0.278033
3	16	0	1.690509	3.966470	-0.278860
4	7	0	-1.347756	1.380480	0.281447
5	7	0	1.347790	1.380264	-0.282068
6	7	0	-0.640471	-0.566355	-1.984569
7	7	0	0.640423	-0.565548	1.984605
8	6	0	-0.710388	2.526461	0.132681
9	6	0	1.377681	-1.918760	-0.165387
10	6	0	-2.042766	-2.246307	-1.046019
11	6	0	2.700498	1.580623	-0.534644
12	6	0	0.710599	2.526356	-0.133436
13	6	0	-0.614337	0.057848	-4.299824
14	1	0	-0.192106	0.678899	-5.081302
15	6	0	-1.616101	-0.879927	-4.566129
16	1	0	-1.999551	-1.006930	-5.573577
17	6	0	0.614570	0.059820	4.299556
18	1	0	0.192407	0.681255	5.080768
19	6	0	3.083519	2.944895	-0.568442
20	6	0	3.044128	-3.231233	1.078549
21	1	0	3.553478	-3.473577	2.006617
22	6	0	-1.618013	-1.492761	-2.224492
23	6	0	-3.044489	-3.231373	-1.077380
24	1	0	-3.553889	-3.474029	-2.005341
25	6	0	-2.114475	-1.652944	-3.526816
26	1	0	-2.887199	-2.387824	-3.716441
27	6	0	3.392823	-3.910524	-0.083363
28	1	0	4.164634	-4.672996	-0.057908
29	6	0	2.042538	-2.246048	1.046763
30	6	0	1.617937	-1.491891	2.224901
31	6	0	-0.157061	0.181194	-2.997003
32	1	0	0.623627	0.884444	-2.734768
33	6	0	-2.700413	1.581080	0.534049

Table S8. Optimized Atomic coordinates obtained from DFT calculations of $[2]^+$.

34	6	0	-1.377918	-1.918547	0.166008
35	6	0	1.740361	-2.628209	-1.318928
36	1	0	1.247629	-2.420875	-2.263389
37	6	0	2.114574	-1.651393	3.527239
38	1	0	2.887333	-2.386160	3.717143
39	6	0	-3.393312	-3.910078	0.084837
40	1	0	-4.165230	-4.672453	0.059704
41	6	0	-1.740745	-2.627394	1.319872
42	1	0	-1.248032	-2.419653	2.264253
43	6	0	-3.083209	2.945427	0.567742
44	6	0	2.735944	-3.608067	-1.280578
45	1	0	2.998194	-4.142208	-2.189807
46	6	0	1.616355	-0.877824	4.566218
47	1	0	1.999955	-1.004302	5.573674
48	6	0	0.157147	0.182519	2.996725
49	1	0	-0.623571	0.885645	2.734244
50	6	0	-2.736445	-3.607148	1.281940
51	1	0	-2.998809	-4.140826	2.191407
52	6	0	3.665281	0.583200	-0.759065
53	6	0	4.974820	0.973162	-0.999575
54	1	0	5.730825	0.214745	-1.174517
55	1	0	4.685648	4.380889	-0.831629
56	6	0	4.402669	3.334070	-0.809608
57	6	0	5.342839	2.331653	-1.022514
58	6	0	-3.665363	0.583827	0.758535
59	6	0	-4.974826	0.974019	0.999056
60	1	0	-5.730967	0.215752	1.174061
61	1	0	-4.685112	4.381694	0.830820
62	6	0	-4.402307	3.334823	0.808893
63	6	0	-5.342631	2.332580	1.021890
64	1	0	3.378370	-0.460322	-0.746447
65	1	0	6.376002	2.604212	-1.212268
66	1	0	-3.378623	-0.459738	0.745984
67	1	0	-6.375749	2.605301	1.211645

Table S9. Optimized Atomic coordinates obtained from DFT calculations of $[\mathbf{R1}]^+$.

Center Atomic Atomic Coordinates (Angstroms)

Number	N	lumber	Туре	X Y	Z
1	6	0	1.645524	-0.688774	1.057703
2	6	0	1.320067	1.218175	-1.032447
3	6	0	2.222796	-0.137520	2.211030
4	1	0	1.846155	0.797719	2.613898
5	6	0	3.291034	-0.764800	2.857217
6	1	0	3.720901	-0.312640	3.747010
7	6	0	3.816617	-1.964200	2.365846
8	1	0	4.647486	-2.447030	2.870206
9	6	0	3.268253	-2.533329	1.222396
10	1	0	3.680281	-3.464416	0.844339
11	6	0	2.193928	-1.905623	0.568290
12	6	0	1.565831	-2.440136	-0.638807
13	6	0	1.955433	-3.602778	-1.321922
14	1	0	2.790331	-4.184159	-0.950100
15	6	0	1.282716	-4.001547	-2.467842
16	1	0	1.588189	-4.899063	-2.996419
17	6	0	0.212332	-3.231855	-2.933308
18	1	0	-0.339289	-3.502846	-3.826171
19	6	0	-0.136796	-2.093040	-2.224658
20	1	0	-0.952689	-1.456824	-2.545225
21	6	0	2.080424	0.902389	-2.168379
22	1	0	2.068618	-0.107292	-2.567060
23	6	0	2.870601	1.864109	-2.802624
24	1	0	3.450060	1.589489	-3.679985
25	6	0	2.927532	3.174083	-2.315621
26	1	0	3.543765	3.917749	-2.810645
27	6	0	2.190680	3.516310	-1.188065
28	1	0	2.240613	4.533969	-0.811902
29	6	0	1.393959	2.551805	-0.546563
30	6	0	0.593260	2.834717	0.643099
31	6	0	0.535887	4.062341	1.321455
32	1	0	1.123101	4.897798	0.960164
33	6	0	-0.258653	4.203842	2.449746
34	1	0	-0.297848	5.152955	2.974968
35	6	0	-1.002092	3.109305	2.901832
36	1	0	-1.633226	3.172453	3.780784
37	6	0	-0.913563	1.918133	2.198851
38	1	0	-1.460999	1.037232	2.511089

39	6	0	-1.900456	1.419959	-2.056745
40	1	0	-0.957028	1.844808	-2.382242
41	6	0	-3.108470	1.778067	-2.646994
42	1	0	-3.121403	2.499035	-3.456734
43	6	0	-4.281373	1.195352	-2.170066
44	1	0	-5.244039	1.451434	-2.600683
45	6	0	-4.204200	0.278913	-1.125118
46	1	0	-5.110080	-0.172072	-0.739661
47	6	0	-2.957420	-0.042927	-0.575757
48	6	0	-2.788209	-1.004546	0.542640
49	6	0	-3.847824	-1.742675	1.082589
50	1	0	-4.849591	-1.642508	0.684025
51	6	0	-3.610310	-2.620788	2.136564
52	1	0	-4.426278	-3.197443	2.560187
53	6	0	-2.314095	-2.747369	2.632403
54	1	0	-2.082220	-3.419419	3.451069
55	6	0	-1.302571	-1.990340	2.049826
56	77	0	0.057818	0.007896	-0.000030
57	7	0	0.513916	-1.701840	-1.110213
58	7	0	-0.142352	1.775660	1.101989
59	7	0	-1.821540	0.531206	-1.050982
60	7	0	-1.528197	-1.139113	1.033636
61	1	0	-0.274624	-2.049828	2.390996

Photoluminescence in thin film:

Thin film	$\lambda_{\rm em} / {\rm nm}^b$	$\Phi_{ m PL}$ / % c	τ / ns^d
1 :[Bmim][PF ₆]	658	14	257
2 :[Bmim][PF ₆]	707	5	117

Table S10. Photophysical properties of complex 1 and 2 in doped thin film.^a

^{*a*}Photophysical properties measured on a quartz/thin film. ^{*b*} $\lambda_{exc} = 320$ nm. ^{*c*} Φ_{PL} measured using an integrating sphere. ^{*d*} $\lambda_{exc} = 340$ nm.



Fig. S11: Photoluminescence spectrum for **1** and **2** in thin film: **Quartz / 1 or 2:[Bmim][PF**₆] upon excitation at 320 nm. [Bmim][PF₆] is 1-butyl-3-methylimidazolium hexafluorophosphate.

Device characteristics:



Fig. S12: Device performance *versus* time (a) LEEC-1 and (b) LEEC-2 under a pulsed current of 800 A m⁻² (average current density), 1KHz and 50% of duty cycle.

Table S11: Device performance for LEEC-1 under pulsed current of 400 and 800 A m^{-2} (average current density).

Device	PC / A m ⁻²	Luminance _{max} ^a / cd m ⁻²	<i>t</i> _{1/2} ^b / h	EQE _{max} ^c / %	λ _{em} ^{max} EL / nm	CIE ^d
LEEC-1	400	59	0.24	0.23	661	0.65, 0.34
	800	72	0.15	0.13	001	

^{*a*}Maximum luminance. ^{*b*}Time to reach one-half of the maximum luminance. ^{*c*}Maximum external quantum efficiency. ^{*d*}Commission internationale de l'Éclairage.

Device	PC / A m ⁻²	Light output _{max} ^a /µW cm ⁻²	<i>t</i> _{1/2} ^{<i>b</i>} / h	EQE _{max} ^c / %	λ _{em} ^{max} EL / nm
LEEC- 2	400	262	80	0.37	705
	800	471	>80	0.33	/05

Table S12: Device performance for LEEC-2 under pulsed current of 400 and 800 A m⁻².

^{*a*}Maximum light output. ^{*b*}Time to reach one-half of the maximum light output. ^{*c*}Maximum external quantum efficiency.

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