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PAPER

## Efficient orange light-emitting electrochemical cells†

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We report the first bis-cyclometalated cationic iridium(III) complex with *N*-aryl-substituted 1*H*-imidazo[4,5-*f*][1,10]phenanthroline. The complex emits yellow-orange phosphorescence with a maximum at 583 nm, a quantum yield of 43%, and an excited-state lifetime of 910 ns in argon-saturated dichloromethane. Optimized orange light-emitting electrochemical cells with the new Ir(III) complex exhibit fast turn-on, a peak luminance of 684 cd m<sup>-2</sup> and a peak efficacy of 6.5 cd A<sup>-1</sup>; in 850 h of continuous operation their luminance and efficacy decrease only by 20%.

## Introduction

Light-emitting electrochemical cells (LEC)<sup>1</sup> are electroluminescent devices that require only an ionic transition metal complex (iTMC) to transport charges and to emit light.<sup>2-4</sup> Solution-processed LEC with an ionic emitting layer offer advantages over organic light-emitting diodes (OLED), namely, compatibility with air-stable cathodes, simple architecture and cheap production;<sup>4-6</sup> moreover, LEC can perform efficiently at voltages as low as the redox gap of the emitter (<3.5 V for visible light).<sup>2</sup>

At the present stage of development, however, LEC have longer turn-on time (*t*<sub>on</sub>), shorter lifetime (*t*<sub>1/2</sub>, the time it takes for the luminance to decrease to half of its maximum value), and lower efficiency<sup>4</sup> than OLED do.<sup>7</sup> Typical LEC exhibit *t*<sub>on</sub> ranging from minutes to days and *t*<sub>1/2</sub> < 100 h.<sup>4</sup> The record *t*<sub>1/2</sub> for LEC is 4000 h;<sup>8</sup> for comparison, the best OLED exhibit *t*<sub>1/2</sub> > 10<sup>5</sup> h.<sup>7</sup>

A range of emission colours, including white,<sup>9</sup> and efficacies of up to 38 lm W<sup>-1</sup> were achieved with iridium(III) iTMC LEC.<sup>4,8-15</sup> Although relatively stable, efficient and bright LEC were reported, their turn-on times were hours-long.<sup>13-15</sup> The known fast LEC are not stable.<sup>16</sup> Recently, a pulsed current driving provided fast and stable LEC;<sup>8</sup> however, their efficacy was only 3.6 cd A<sup>-1</sup>. LEC performance is not limited by the charge injection from the contacts, but by the photophysical<sup>17</sup> and charge-transport<sup>18</sup> properties of the iTMC; therefore, the design of the new iTMC is crucial for LEC development.<sup>4</sup>

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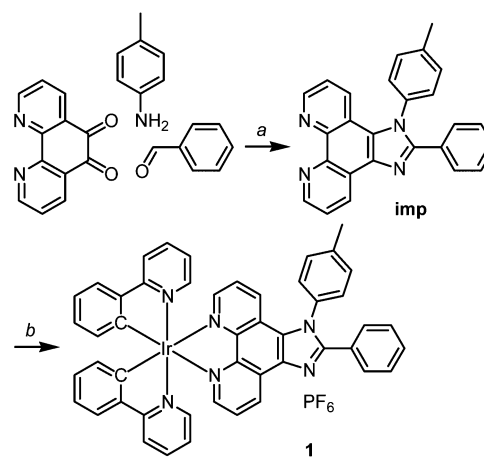
† Electronic supplementary information (ESI) available: Synthesis of [(ppy)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub>; NMR spectra; experimental techniques; crystallographic data; absorption maxima and *ε*; excitation spectra; emission decay trace; performance of LEC devices with 100/150/190 nm emitting layers. CCDC 876632. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm33969b

Here, we report orange light-emitting electrochemical cells that employ a new phosphorescent cationic Ir(III) complex (**1**, Scheme 1). These LEC exhibit fast turn-on, high luminance and efficacy, and long lifetime.

## Results and discussion

## Synthesis and characterization

The new bidentate 1*H*-imidazo[4,5-*f*][1,10]phenanthroline ligand **imp** (Scheme 1) was obtained in a one-step reaction<sup>19,20</sup> of 1,10-phenanthroline-5,6-dione,<sup>21</sup> benzaldehyde, 4-methylaniline and ammonium acetate in acetic acid at reflux (24 h) in 67% yield on a 1 g scale after re-crystallization. We chose ligand **imp** because it contains a strong metal-binding 1,10-phenanthroline heterocycle fused with imidazole and because one can adjust the steric and electronic properties of **imp** by changing the substituents at the N1 and C2 positions of the imidazole.<sup>19,20,22,23</sup>



**Scheme 1** Synthesis of ligand **imp** and complex **1**. Reaction conditions: (a) ammonium acetate, acetic acid, reflux, 24 h, under Ar; (b) [(ppy)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH, 40 °C, 24 h, under Ar, KPF<sub>6</sub>.

We prepared complex **1** (Scheme 1) from  $[(ppy)_2Ir(\mu-Cl)]_2$  ( $ppy = N,C^{2'}-2$ -phenylpyridyl) and **imp** in 65% yield on a 0.5 g scale after chromatography on silica and after re-crystallization. **1** was characterized by elemental analysis,  $^1H$ ,  $^{13}C$  and  $^{19}F$  NMR spectroscopy, mass-spectrometry and X-ray crystallography.

Fig. 1 shows the crystal structure of **1** (Table S1, ESI†). The Ir(III) ion is in a distorted octahedral  $[(C^{\wedge}N)_2Ir(N^{\wedge}N)]^+$  coordination environment with the two nitrogen atoms of the  $C^{\wedge}N$  ligands in *trans*-position to each other. The Ir–N bonds to the  $C^{\wedge}N$  ligands [2.042(4) Å, 2.050(3) Å] are shorter than the ones to the  $N^{\wedge}N$  ligands [2.126(4) Å, 2.143(3) Å] (Table S2, ESI†).

The  $C^{\wedge}N$  ligands in **1** are planar and the dihedral angle between the phenyl and pyridyl rings is less than  $5.7^\circ$ . The fused core of **imp** is planar; however, both of its aryl substituents are out of plane with a dihedral angle to the imidazole of  $29^\circ$  (phenyl) and  $88^\circ$  (4-methylphenyl). These aryl substituents prevent intermolecular face-to-face  $\pi$ – $\pi$  stacking of **1** through **imp**. The structural features of **imp** in **1** are similar to those reported for its non-coordinated analogs.<sup>20</sup> The co-crystallized water molecule (half per asymmetric unit of **1**) forms a hydrogen bond with the N3 atom of imidazole with an  $O\cdots N$  distance of 2.797(9) Å. Inter-metallic communication in **1** is prevented by the long Ir $\cdots$ Ir distance, 8.5538(15) Å.

We note that **1** is the first metal complex with an *N*-aryl substituted 1*H*-imidazo[4,5-*f*][1,10]phenanthroline. Previous reports discussed either the non-coordinated analogs of **imp**<sup>20</sup> or Ir(III) complexes with *N*-H<sup>22,23</sup> and *N*-alkyl<sup>22</sup> 1*H*-imidazo[4,5-*f*][1,10]phenanthrolines.

### Electrochemistry

The redox potentials of **1** (relative to  $Fc^+/Fc$ ) were measured with cyclic voltammetry (Fig. 2 and Table 1). Complex **1** in acetonitrile undergoes a reversible reduction of **imp** at  $-1.76$  V and a quasi-reversible oxidation of the Ir–phenyl fragment at  $0.88$  V.<sup>22</sup> The redox gap of **1**,  $\Delta E = E_{1/2}^{ox} - E_{1/2}^{red}$ , is 2.64 V. The redox properties of **1** in DMF are similar to those in acetonitrile (Fig. 2 and Table 1).

### Optical spectroscopy

Complex **1** is a yellow solid that gives yellow solutions in polar organic solvents. The lowest-energy electronic band of **1** in

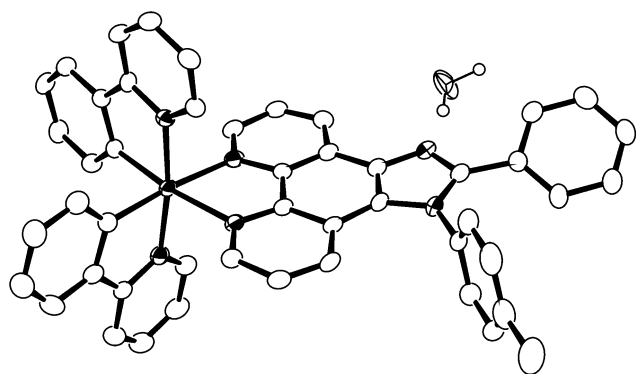


Fig. 1 Structure of **1** [CCDC 876632; 50% probability ellipsoids; H atoms (except for the water molecule) and  $PF_6^-$  anion omitted; ORTEP]. Heteroatoms are shown as octant ellipsoids: Ir and N, black; O, clear.

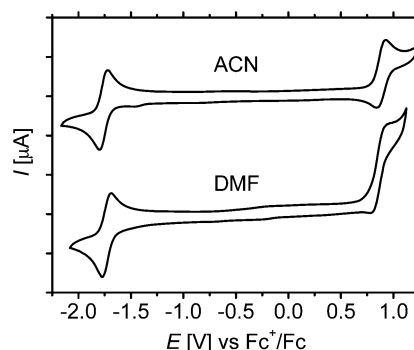


Fig. 2 Cyclic voltammograms of **1** in acetonitrile and DMF (glassy carbon electrode, 0.1 M  $NBu_4PF_6$ ,  $100\text{ mV s}^{-1}$ ). The unit on the vertical axis is  $10\text{ }\mu\text{A}$ .

dichloromethane is observed at  $\lambda > 450$  nm with molar absorption coefficients  $\epsilon < 1.4 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$ ; we assign this band to an (Ir–phenyl)-to-**imp** charge transfer transition<sup>10,22</sup> (Fig. 3 and Table S3, ESI†). The intense absorption bands of **1** at  $\lambda < 450$  nm with  $\epsilon = (9.5\text{--}84) \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$  are assigned to MLCCT/ILCT and ligand  $\pi$ – $\pi^*$  transitions (Fig. 3 and Table S3, ESI†).

**1** exhibits yellow-orange phosphorescence in argon-saturated dichloromethane solution with a maximum ( $\lambda_{max}$ ) at 583 nm, a quantum yield ( $\Phi$ ) of 43%, and an excited-state lifetime ( $\tau$ ) of 910 ns (Fig. 4). The excitation spectrum of **1** matches its absorption spectrum (Fig. S1, ESI†). The luminescence decay of **1** is a single exponential function suggesting the presence of one emissive centre in solution (Fig. S2, ESI†). The lack of vibronic structure in the phosphorescence spectrum and the relatively short calculated radiative lifetime ( $\tau_{rad} = \tau/\Phi = 2.1\text{ }\mu\text{s}$ ) indicate that **1** emits from a charge-transfer [(Ir–phenyl)-to-**imp**] excited state.<sup>10,22</sup> The calculated radiative and non-radiative rate constants of **1** are  $k_{rad} = \Phi/\tau = 4.7 \times 10^5\text{ s}^{-1}$  and  $k_{nr} = (1 - \Phi)/\tau = 6.3 \times 10^5\text{ s}^{-1}$ .

**1** exhibits a broad emission spectrum with a maximum at 590 nm and a quantum yield of 45% in thin films that have **1** and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM- $PF_6$ ) in a 4 to 1 molar ratio (Fig. 4).

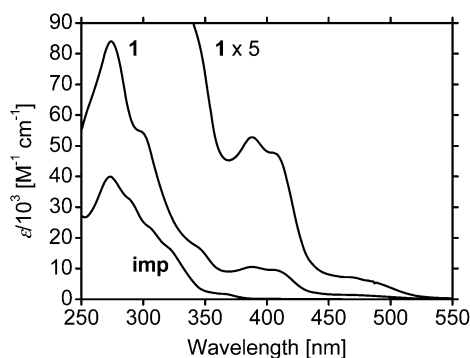
### Electroluminescence

Complex **1** has two characteristics that are essential for an efficient electroluminescence emitter: (i) high phosphorescence quantum yield and (ii) fast radiative decay (short  $\tau_{rad}$ ).<sup>4</sup>

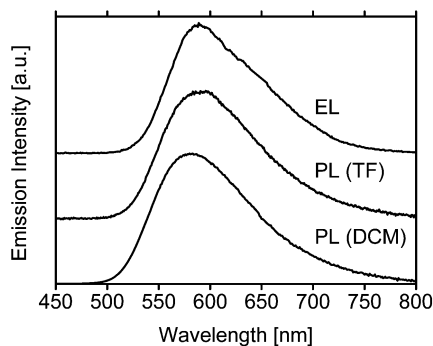
Table 1 Redox properties of **1**<sup>a</sup>

Solvent	$E_{1/2}^{ox}/V$	$E_{1/2}^{red}/V$	$\Delta E/V^b$
ACN	0.88 (83) <sup>c</sup>	–1.76 (73)	2.64
DMF	0.95 <sup>d</sup>	–1.73 (78)	2.68

<sup>a</sup> Relative to  $Fc^+/Fc$ . On a glassy carbon working electrode, in the presence of 0.1 M  $(NBu_4)PF_6$ , at a scan rate of  $100\text{ mV s}^{-1}$ . Estimated error:  $\pm 50$  mV. The anodic/cathodic peak separation for the reversible and quasi-reversible processes is given in mV within parentheses (for the standard,  $Fc^+/Fc$  couple, it was 78 mV). <sup>b</sup>  $\Delta E = E_{1/2}^{ox} - E_{1/2}^{red}$ . <sup>c</sup> Quasi-reversible process. <sup>d</sup> Irreversible process; the oxidation peak potential is reported.



**Fig. 3** Absorption spectra of ligand **imp** ( $2.26 \times 10^{-4}$  M) and complex **1** ( $7.58 \times 10^{-5}$  M) in dichloromethane.

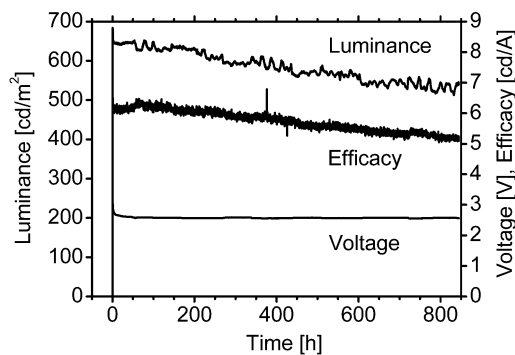
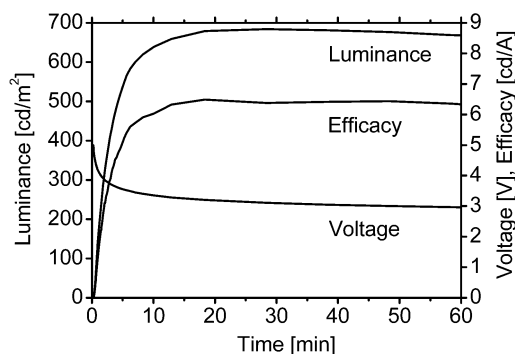


**Fig. 4** Corrected and normalized photoluminescence (PL) and electroluminescence (EL) spectra of **1** at room temperature. PL (DCM): argon-saturated dichloromethane,  $10^{-5}$  M,  $\lambda_{\text{exc}} = 350$  nm,  $\Delta\lambda_{\text{em}} = 1$  nm. PL (TF): thin film **1**: BMIM-PF<sub>6</sub> (4 : 1). EL: ITO/PEDOT:PSS/**1**: BMIM-PF<sub>6</sub> (4 : 1; 150 nm)/Al.

We investigated the electroluminescence performance of **1** in light-emitting electrochemical cells. A 90 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated on top of a patterned indium-tin-oxide-coated glass substrate followed by a 150 nm emitting layer of **1** and BMIM-PF<sub>6</sub> in a 4 to 1 molar ratio (the ionic liquid was added to reduce the turn-on time of the device<sup>24</sup>). A vapour-deposited 70 nm Al layer served as the top electrode. The devices were operated with a block-wave pulsed current driving<sup>8</sup> at 1000 Hz with a duty cycle of 50% and a current of  $102 \text{ A m}^{-2}$  (averaged over 'pulse' and 'no-pulse' time,  $2\sigma = 4 \text{ A m}^{-2}$ ;  $\approx 200 \text{ A m}^{-2}$  per pulse).

The electroluminescence spectrum of **1** in LEC (Fig. 4) matches its photoluminescence spectrum in thin film (Fig. 4) and has a maximum at 589 nm and CIE coordinates (0.55, 0.44) that correspond to an orange emission. Fig. 5 shows a typical time-dependence of the luminance, voltage and efficacy in an optimized device. Although the operating voltage is initially 5 V, after 2 min and 50 min it decreases to 4 V and 3 V, respectively, and finally, after 50 h, it stabilizes at 2.6 V (Fig. 5), a value that is equal to the redox gap of **1** determined from cyclic voltammetry (Table 1).<sup>2</sup>

The device response is fast: it takes only 45 s to reach the luminance of  $100 \text{ cd m}^{-2}$ , and 28 min to reach the peak luminance of  $684 \text{ cd m}^{-2}$  (Fig. 5). The peak efficacy of the device is



**Fig. 5** Time-dependence of the luminance, voltage and efficacy of a LEC device ITO/PEDOT:PSS/**1**: BMIM-PF<sub>6</sub> (4 : 1; 150 nm)/Al. Top: the first 60 min of the experiment. Bottom: the 850 h experiment (the spikes in the efficacy plot are caused by fluctuations in the current).

$6.5 \text{ cd A}^{-1}$  (Fig. 5), which is 1.8-times higher than that of the reported analog.<sup>8</sup> To explain the difference in the efficacies of these devices we note that in the thin film with the ionic liquid **1** exhibits 1.9-times higher phosphorescence quantum yield than does the emitter<sup>14</sup> used in the analog LEC.<sup>8</sup>

The device is relatively stable: its luminance and efficacy decrease only by 20% in 850 h (35 days) of continuous operation (Fig. 5). Linear extrapolation of the time dependence of luminance provides the value of  $t_{1/2} = 2000$  h, which is a remarkable result for LEC<sup>4</sup> (but, clearly, a long way from matching OLED performance<sup>7</sup>). We note that the only other emitters that gave  $t_{1/2}$  similar to that of **1** in LEC are the Ir(III) complexes with sterically hindered (at the coordination site) N<sup>N</sup> ligands.<sup>8,13,14</sup>

The peak luminance and efficacy of LEC device become higher when the thickness of the emitting layer (**1**: BMIM-PF<sub>6</sub>, 4 : 1) is increased from 100 nm ( $560 \text{ cd m}^{-2}$  and  $5.4 \text{ cd A}^{-1}$ ) to 150 nm ( $684 \text{ cd m}^{-2}$  and  $6.5 \text{ cd A}^{-1}$ ) and to 190 nm ( $975 \text{ cd m}^{-2}$  and  $9.3 \text{ cd A}^{-1}$ ) (all of these LEC were operated under the same conditions; Fig. S3, ESI†). These gains, however, come at a price of higher driving voltage that goes up from 2.6 V at 100/150 nm to 2.9 V at 190 nm (these data refer to the voltage after 50 h of continuous operation; Fig. S3, ESI†). The shorter lifetimes ( $t_{1/2}$  from linear extrapolation) of both the 100 nm (320 h) and 190 nm (180 h) LEC when compared with the 150 nm one (2000 h) are likely to be caused by the faster decomposition of **1** on the interfaces in the 100 nm LEC or by the higher driving voltage<sup>2</sup> required in the 190 nm LEC (Fig. 5 and S3, ESI†).

## Conclusions

We made fast, efficient and long-lived orange light-emitting electrochemical cells with a new cationic Ir(III) complex **1**. We consider that the performance of **1** in LEC is determined by the ligand **imp** that combines a metal-binding rigid 1*H*-imidazo[4,5-*f*][1,10]phenanthroline chromophore core,<sup>22,23</sup> charge-transporting conjugated nitrogen heterocycle and aryls,<sup>18</sup> and solubilizing out-of-plane aryl groups (Scheme 1 and Fig. 1). The performance of LEC results from a combination of pulsed current driving,<sup>8</sup> the use of an ionic liquid<sup>24</sup> and the design of the new emitter **1**. The facile synthesis of *N*-aryl substituted **imp** ligands opens the way to new electroluminescent metal complexes for lighting and display applications.

## Experimental

### Materials and methods

Elemental analyses were performed by Dr E. Solari, Service for Elemental Analysis, Institute of Chemical Sciences and Engineering (ISIC EPFL). <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra were recorded with AV400, AVIII-400, and Ascend 400 spectrometers (400 MHz, Bruker). Mass spectra were recorded with Q-TOF Ultima (Waters) and TSQ7000 (Thermo Fisher) spectrometers (Mass-Spectroscopy Service, ISIC EPFL).

Purification, crystal growth, and handling of all compounds were carried out under air. All products were stored in the dark. Chemicals from commercial suppliers were used without purification. Chromatography was performed on a column with an i.d. of 30 mm on silica gel 60 (Fluka, Nr 60752). The progress of reactions and the elution of products were followed on TLC plates (silica gel 60 F<sub>254</sub> on aluminum sheets, Merck).

### Synthesis of ligand **imp**

The reaction was performed under argon. The solvents were deoxygenated by bubbling with Ar, but they were not dried. Benzaldehyde (0.22 mL, 227 mg, 2.14 mmol; Fluka) and 4-methylaniline (229 mg, 2.14 mmol; Aldrich) were dissolved in acetic acid (10 mL) and stirred for 10 min at room temperature to give a yellow solution. 1,10-Phenanthroline-5,6-dione<sup>21</sup> (450 mg, 2.14 mmol) and ammonium acetate (1.65 g, 21.4 mmol, excess) were added. The reaction mixture was refluxed for 24 h to give a dark red solution. It was cooled to room temperature, diluted with water (20 mL), and neutralized with NH<sub>4</sub>OH to give an oily precipitate of the product. The reaction mixture was extracted with water and CH<sub>2</sub>Cl<sub>2</sub>. The yellow organic layer was washed with water and evaporated to dryness to give red oil. It was re-dissolved in a minimum volume of CH<sub>2</sub>Cl<sub>2</sub>. Acetone (20 mL) was added. Rotary evaporation removed CH<sub>2</sub>Cl<sub>2</sub> and left a suspension of the product in acetone. It was cooled to -15 °C for 2 h and filtered. The product was washed with hexane. The re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>-acetone was repeated one more time to give the product as a white solid: 438 mg (1.12 mmol, 52%). Anal. calcd for C<sub>26</sub>H<sub>18</sub>N<sub>4</sub>·0.3H<sub>2</sub>O (MW 392.45): C, 79.57; H, 4.79; N, 14.28. Found: C, 79.65; H, 4.65; N, 13.98%. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 9.10 (dd, *J* = 4.4, 2.0 Hz, 1H), 9.03 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.97 (dd, *J* = 4.4, 2.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.67–7.59 (m, 4H), 7.55–7.48 (m, 3H), 7.45–7.36

(m, 4H) ppm: 3H of the CH<sub>3</sub> group are obscured by the solvent signal. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.22 (dd, *J* = 4.4, 1.6 Hz, 1H), 9.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 9.09 (dd, *J* = 4.4, 1.6 Hz, 1H), 7.79 (dd, *J* = 8.0, 4.4 Hz, 1H), 7.66–7.61 (m, 2H), 7.54 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.48–7.40 (m, 4H), 7.40–7.32 (m, 4H), 2.58 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): all of the expected signals in the aromatic (21C) and aliphatic (1C) regions were observed, δ = 152.3, 149.0, 147.9, 144.9, 144.4, 140.5, 136.1, 135.3, 131.1, 130.5, 130.0, 129.3, 129.3, 128.5, 128.4, 128.1, 127.0, 124.1, 123.5, 122.1, 119.6, 21.5 (CH<sub>3</sub>) ppm. ESI<sup>+</sup> TOF MS: *m/z* 387.7 (*M* + H)<sup>+</sup>, 100%. For the scaled-up procedure, benzaldehyde (0.44 mL, 462 mg, 4.31 mmol), 4-methylaniline (458 mg, 4.32 mmol), acetic acid (15 mL), 1,10-phenanthroline-5,6-dione (900 mg, 4.28 mmol), and ammonium acetate (3.3 g, 42.8 mmol) gave 1.13 g (2.88 mmol, 67%) of the product after two re-crystallizations (acetone, 2 × 20 mL). We note that the reported *N*-aryl substituted 1*H*-imidazo[4,5-*f*][1,10]phenanthrolines<sup>20</sup> (analogs of **imp**) were synthesised in a similar way to ours, but at lower temperatures (at reflux in ethanol), and in those cases the reactions took a week to complete;<sup>20</sup> in contrast, with our procedure the reaction was complete in one day.

### Synthesis of complex **1**

The reaction was performed under argon. The solvents were deoxygenated by bubbling with Ar, but they were not dried. [(ppy)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (200 mg, 0.187 mmol, small excess) and ligand **imp** (144 mg, 0.373 mmol) in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (40/5 mL) were stirred overnight at 40 °C to give an orange solution. It was evaporated to dryness. The residue was purified by column chromatography (silica, 20 g). Elution with 2.0–3.0% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub> removed the impurities. Elution with 4.0–5.0% CH<sub>3</sub>OH in CH<sub>2</sub>Cl<sub>2</sub> recovered the product as a yellow eluate. The desired fractions were evaporated to dryness, re-dissolved in CH<sub>3</sub>OH (5 mL), and added drop-wise to a stirred aqueous solution of KPF<sub>6</sub> (1.07 g, 5.8 mmol, in 25 mL of water, excess; Alfa Aesar) in order to convert the complex to the hexafluorophosphate salt. The resulting suspension was stirred for 1 h and filtered. The complex was washed with water and ether. It was re-crystallized by pouring its solution in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) to ether (70 mL). The complex was filtered and washed with ether. Yellow solid: 244 mg (0.232 mmol, 62%). Anal. calcd for C<sub>48</sub>H<sub>34</sub>F<sub>6</sub>IrN<sub>6</sub>P·H<sub>2</sub>O (MW 1050.02): C, 54.90; H, 3.46; N, 8.00. Found: C, 54.75; H, 3.57; N, 7.85%. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 9.55 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.39 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.27 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.05–7.97 (m, 2H), 7.95 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.86–7.69 (m, 7H), 7.60–7.38 (m, 10H), 7.21–7.12 (m, 2H), 7.08–6.99 (m, 2H), 6.94–6.85 (m, 2H), 6.48–6.42 (m, 2H), 2.60 (s, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): all of the expected signals in the aromatic (43C) and aliphatic (1C) regions were observed, δ = 167.90, 167.79, 154.65, 150.19, 149.74, 149.58, 148.73, 148.61, 148.46, 145.05, 144.78, 143.87, 143.80, 141.85, 138.20, 137.74, 136.98, 134.12, 132.74, 131.79, 131.77, 131.71, 131.61, 130.78, 130.71, 130.39, 130.05, 129.38, 129.19, 128.53, 128.12, 128.02, 127.90, 126.84, 126.79, 125.91, 124.95, 124.93, 123.26, 123.12, 122.80, 122.73, 119.88, 21.26 (CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (376 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = -73.60 (d, *J*<sub>P-F</sub> = 710 Hz, PF<sub>6</sub>) ppm. ESI<sup>+</sup> TOF MS: *m/z* 887.24 (*M* - PF<sub>6</sub>)<sup>+</sup>, 100%. For the scaled-up procedure, [(ppy)<sub>2</sub>Ir(μ-Cl)]<sub>2</sub> (400 mg, 0.37 mmol) and **imp** (283 mg,



0.73 mmol) in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (40/5 mL) gave 504 mg (0.48 mmol, 65%) of the product after chromatography (silica, 20 g), anion exchange (CH<sub>3</sub>OH, 10 mL; KPF<sub>6</sub>, 3.7 g, 20 mmol, in 50 mL of water), and re-crystallization (15 mL of CH<sub>2</sub>Cl<sub>2</sub>-200 mL of ether). It is important not to use an excess of ligand **imp** in the reaction, because **imp** co-elutes with **1** during chromatography, and it can be removed only by repeated re-crystallization from CH<sub>2</sub>Cl<sub>2</sub>-ether.

### Electroluminescence devices

The solvents were supplied by Aldrich. The thickness of films was determined with an Ambios XP-1 profilometer. Indium tin oxide ITO-coated glass plates (15 Ω<sup>-1</sup>) were patterned by conventional photolithography (Naranjo Substrates). The substrates were cleaned by sonication in water-soap, water, and 2-propanol baths, in that order. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 min.

The electroluminescence devices were made as follows. First, a 90 nm layer of PEDOT:PSS (CLEVIOS™ P VP AI 4083, aqueous dispersion, 1.3–1.7% solid content, Heraeus) was spin-coated on the ITO glass substrate to improve the reproducibility of the devices and to prevent the formation of pinholes. Then, a 100/150/190 nm transparent film of **1** and the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (>98.5%, Sigma-Aldrich) in a 4 to 1 molar ratio were spin-coated from 20 mg mL<sup>-1</sup> (**1**) acetonitrile solution at 1000 rpm for 20 s. The device was transferred into an inert atmosphere glovebox (<0.1 ppm O<sub>2</sub> and H<sub>2</sub>O, M. Braun) and dried on a hot plate at 100 °C for 1 h. The Al electrode (70 nm) was thermally vapor-deposited using a shadow mask under a vacuum (<1 × 10<sup>-6</sup> mbar) with an Edwards Auto500 evaporator integrated in the glovebox. The area of the device was 6.5 mm<sup>2</sup>. The devices were not encapsulated and were characterized inside the glovebox at room temperature. The device lifetime was measured by applying pulsed currents and monitoring the voltage and luminance by a True Colour Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System.

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