Introduction

Light-emitting electrochemical cells (LECs) are promising electroluminescent devices for highly efficient and low-cost applications in ultrathin and flexible lighting. The charged active layer sandwiched between two electrodes is either a conjugated light-emitting polymer\(^1\) or an ionic transition-metal complex (iTMC).\(^2\) The ionic nature of the active material allows the charged species to migrate towards the electrodes when a bias is applied, forming doped zones and thus lowering the injection barrier facilitating efficient electron and hole injection.\(^3\)

Due to their particular stability, extremely high efficiencies and ability to tune the emission color, iTMCs incorporating iridium(III) (Ir-iTMCs) are by far the most versatile active materials used in iTMC-LECs.\(^4\) Ir-iTMCs are typically of the form \([\text{Ir}(\text{C}^\text{N})_2(\text{N}^\text{N})]^+\), where \(\text{C}^\text{N}\) is a cyclometallating ligand and \(\text{N}^\text{N}\) is an \(\text{N},\text{N}\)-chelate. Since the high spin–orbit coupling of Ir-iTMCs permits intersystem-crossing from singlet to triplet states, iridium(III)-based materials achieve spin-forbidden phosphorescence emissions approaching photoluminescence quantum yields of 100%.\(^6,7\) After Slinker et al.\(^8\) reported the first Ir-iTMC-based LEC in 2004, a broad range of stable and efficient Ir-iTMC emitters has been developed, covering the whole visible range.\(^4,7,9\) A major challenge that remains is to attain white light emission.

One approach to white-emitting LECs is to combine blue-green with red-emitting complexes in the active layer of the device or to mix three iTMCs of different colours (blue, red and orange).\(^10\)–\(^13\) Other strategies (not uniquely based on...
Electrospray ionization (ESI) mass spectra were recorded on a Bruker esquire 3000plus instrument. Quantum yields in CH$_2$Cl$_2$ solution and powder were measured using a Hamamatsu absolute photoluminescence (PL) quantum yield spectrometer C11347 Quantaurus-QY. Emission lifetimes and powder emission spectra were measured with a Hamamatsu Compact Fluorescence lifetime Spectrometer C11367 Quantaurus-Tau, using an LED light source with $\lambda_{\text{exc}} = 280$ nm. The preparation of the thin film samples consisted of deposition on a quartz plate (1 cm$^2$) of the complex with addition of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$]. These samples were excited using a light source with $\lambda_{\text{exc}} = 320$ nm at room temperature under ambient conditions.

2,7-Bis[2-(2-hydroxyethoxy)ethoxy]naphthalene$^{20}$ ligands 2-$^5$,2$^6$,2$^7$ and [Ir(ppy)$_2$(4)][PF$_6$]$^{23}$ were prepared by standard procedures. Silica gel 60 was bought from Fluka.

**Compound H$_2$I**

A grey suspension of NaH (232 mg, 5.80 mmol) and 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene (650 mg, 1.93 mmol) were heated in a mixture of 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene,20 ligands 2-$^5$,2$^6$,2$^7$ and [Ir(ppy)$_2$(4)][PF$_6$]$^{23}$ were prepared by standard procedures. Silica gel 60 was bought from Fluka.

**Experimental**

**General**

$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded at room temperature using a Bruker Avance III-600, III-500 or III-400 NMR spectrometer. $^1$H and $^{13}$C NMR chemical shifts were referenced to residual solvent peaks with respect to $\delta$(TMS) = 0 ppm and $^{31}$P NMR chemical shifts with respect to $\delta$(85% aqueous H$_3$PO$_4$) = 0 ppm. Solution absorption and emission spectra were measured using an Agilent 8453 spectrophotometer and a Shimadzu RF-5301PC spectrofluorometer, respectively.

[iTMCs] include multifluorophoric conjugated polymers,14,15 a combined polymer-composite blue-light emitting layer with an orange ionic iridium complex,16,17 or employ a colour conversion layer.18,19 However, all these LEC devices only operate to residual solvent peaks with respect to orange ionic iridium complex,16,17 or employ a colour conversion layer18,19 combined polymer-composite blue-light emitting layer with an orange-emitting [IrTMCs for white-light emission which follows the principle of blue-emitting complexes required for colour-mixing. The reason for the small number and poor performances of white-emitting LECs reported is largely ascribed to the lack of highly efficient and stable deep-blue-emitting complexes required for colour-mixing. We now explore a possible approach to dual-emitting iTMCs for white-light emission which follows the principle of combining complementary colours by combining a blue-emitting naphthalene domain and orange-emitting [Ir(C$^N$$^N$)$_2$] complexes. The naphthalene component is accommodated within a linker between the two cyclometallating units in ligand H$_2$I (Scheme 1).

![Scheme 1](image_url)  
**Scheme 1** Synthesis of cyclometallating ligand H$_2$I with atom labelling for NMR assignments. Conditions: (i) NaH, DMF, 120 °C, 24 h.
filtered and evaporated to dryness. The solid products were combined. The product was purified by column chromato-
graphy (silica, CH₂Cl₂ changing to CH₂Cl₂ : MeOH 100 0 : 1) and [Ir(1)[µ-Cl₂]] was isolated as a yellow solid (90.0 mg, 0.052 mmol, 33.4%). ¹H NMR (500 MHz, CD₃Cl) δ/ppm 9.11
(dd, J = 5.8, 0.9 Hz, 2H, H²⁺), 7.71–7.63 (overlapping m, 4H, H³⁺), 7.56 (d, J = 7.9 Hz, 2H, H²⁺), 7.20 (d, J = 8.7 Hz, 2H, H⁴⁺), 6.97 (dd, J = 8.8, 2.5 Hz, 2H, H⁵⁺), 6.90 (d, J = 2.4 Hz, 2H, H⁶⁺), 6.71 (ddd, J = 7.3, 5.8, 1.4 Hz, 2H, H²⁺), 6.33 (dd, J = 8.5, 2.5 Hz, 2H, H⁴⁺), 5.32 (d, J = 2.6 Hz, 2H, H⁶⁺), 4.04–3.94 (overlapping m, 4H, H⁷⁺), 3.87 (m, 2H, H⁸⁺), 3.81–3.73 (overlapping m, 4H, H⁹⁺), 3.65 (m, 2H, H¹⁰⁺), 3.61–3.57 (overlapping m, 4H, H¹¹⁺). ¹³C NMR (126 MHz, CD₂Cl₂) δ/ppm 168.2 (C²⁺), 159.5 (C⁻⁵⁺), 157.7 (C⁻²⁺), 151.7 (C⁻¹⁺), 147.3 (C²⁺), 137.6 (C¹⁺), 137.0 (C⁶⁺), 136.4 (C⁵⁺), 129.3 (C⁻⁴⁺), 125.3 (C⁻³⁺), 124.9 (C⁻⁷⁺), 121.8 (C⁻⁶⁺), 118.4 (C⁻⁵⁺), 117.2 (C⁻²⁺), 116.6 (C⁻¹⁺), 108.6 (C⁻⁶⁺), 107.5 (C⁻⁵⁺), 70.3 (C⁻³⁺), 70.1 (C⁻⁴⁺), 67.6 (C⁻⁶⁺). ESI-MS m/z 833.5 [Ir(1)]⁻ [base peak, calc. 833.2]. The complex was used in the next step without further purification.

**[Ir(1)(MeOH)][PF₆]⁻**

A yellow suspension of [Ir₂(1)₂[µ-Cl₂]] (188 mg, 0.108 mmol) and AgPF₆ (59.9 mg, 0.237 mmol) in MeOH (10 mL) were stirred at room temperature for 1.5 h. The reaction mixture was filtered over celite, washed with MeOH and evaporated to dryness to give the product as a yellow solid (223 mg, 0.214 mmol, 99.1%). ¹H NMR (500 MHz, CD₃OD) δ/ppm 8.75 (dd, J = 5.8, 1.4, 0.7 Hz, 2H, H²⁺), 7.87 (dd, J = 8.2, 7.5, 1.5 Hz, 2H, H⁴⁺), 7.70–7.63 (overlapping m, 4H, H³⁺), 7.37 (dd, J = 7.3, 5.8, 1.4 Hz, 2H, H⁵⁺), 7.16 (d, J = 8.6 Hz, 2H, H⁶⁺), 6.97 (dd, J = 8.9, 2.5 Hz, 2H, H⁷⁺), 6.89 (d, J = 2.4 Hz, 2H, H⁸⁺), 6.28 (d, J = 8.6, 2.5 Hz, 2H, H⁹⁺), 5.56 (d, J = 2.5 Hz, 2H, H¹⁰⁺), 3.95 (m, 4H, H¹¹⁺), 3.88 (m, 2H, H⁻¹²⁺), 3.83–3.79 (m, 2H, H⁻¹³⁺), 3.76 (m, 2H, H⁻¹⁴⁺), 3.68 (m, 2H, H⁻¹⁵⁺), 3.63 (m, 4H, H⁻¹⁶⁺), 3.34 (s, 6H, H⁻¹⁷⁺). ¹³C NMR (126 MHz, CD₂Cl₂) δ/ppm 168.9 (C¹⁴⁺), 160.5 (C⁻⁸⁺), 158.6 (C⁻⁷⁺), 149.7 (C⁻⁶⁺), 141.0 (C⁻⁵⁺), 139.9 (C⁻⁴⁺), 139.0 (C⁻³⁺), 137.4 (C⁻²⁺), 129.8 (C⁻¹⁺), 126.7 (C⁻¹⁰⁺), 122.6 (C⁻²⁺), 120.0 (C⁻¹¹⁺), 119.6 (C⁻¹²⁺), 117.7 (C⁻¹³⁺), 110.3 (C⁻¹⁴⁺), 108.5 (C⁻¹⁵⁺), 71.1 (C⁺), 68.5 (C⁻¹⁶⁺), 68.4 (C⁻¹⁷⁺), 49.9 (C⁻¹⁸⁺). ESI-MS m/z 833.6 [Ir(1)]⁻ [base peak, calc. 833.2]. The complex was used in the next step without further purification.

**[Ir(1)(2)[µ-Cl₂]]PF₆⁻**

A suspension of [Ir(1)(MeOH)][PF₆]⁻ (141 mg, 0.135 mmol), 2 (42.0 mg, 0.136 mmol) and NH₄PF₆ (220 mg, 1.35 mmol) in MeOH (10 mL) was heated at reflux for 20 h. The orange reaction mixture was filtered through a piece of cotton and the filtrate was evaporated to dryness. The residue was purified by column chromatography (silica, CH₂Cl₂ changing to CH₂Cl₂ : MeOH 100 : 0.25, then to CH₂Cl₂ : MeOH 100 : 1). [Ir(1)(2)][PF₆]⁻ was isolated as an orange solid (96.0 mg, 0.075 mmol, 55.3%). ¹H NMR (500 MHz, CD₃Cl) δ/ppm 8.37 (dd, J = 8.1, 1.2 Hz, 2H, H²⁺), 8.10 (τ, J = 7.9 Hz, 2H, H⁴⁺), 8.06 (dd, J = 5.9, 0.8 Hz, 2H, H⁶⁺), 7.70 (ddd, J = 8.4, 7.5, 1.5 Hz, 2H, H⁸⁺), 7.66 (d, J = 8.8 Hz, 2H, H⁹⁺), 7.30 (overlapping m, 4H, H¹⁰⁺), 7.01 (ddd, J = 7.3, 5.9, 1.4 Hz, 2H, H¹¹⁺), 6.98–6.90 (overlapping m, 6H, H¹²⁺), 6.75–6.69 (overlapping m, 6H, H¹³⁺), 6.55 (br, 4H, H¹⁴⁺), 5.99 (dd, J = 8.6, 2.5 Hz, 2H, H¹⁵⁺), 4.62 (d, J = 2.5 Hz, 2H, H¹⁶⁺), 4.06–3.97 (overlapping m, 4H, H¹⁷⁺), 3.77 (m, 2H, H¹⁸⁺), 3.71 (m, 2H, H¹⁹⁺), 3.66 (m, 2H, H²₀⁺), 3.55 (m, 2H, H²¹⁺), 3.53–3.45 (overlapping m, 4H, H²²⁺). ¹³C NMR (126 MHz, CD₂Cl₂) δ/ppm 168.1 (C¹⁴⁺), 165.7 (C¹³⁺), 159.4 (C¹²⁺), 159.2 (C¹¹⁺), 157.9 (C¹⁰⁺), 150.3 (C⁹⁺), 149.3 (C⁸⁺), 139.8 (C⁷⁺), 138.3 (C⁶⁺), 138.3 (C⁵⁺), 135.4 (C⁴⁺), 130.1 (C³⁺), 129.3 (C²⁺), 128.8 (C¹⁺), 127.9 (C⁰⁺), 127.9 (C⁻¹⁺), 125.9 (C⁻²⁺), 125.0 (C⁻³⁺), 124.7 (C⁻⁴⁺), 121.2 (C⁻⁵⁺), 119.0 (C⁻⁶⁺), 117.3 (C⁻⁷⁺), 116.2 (C⁻⁸⁺), 109.4 (C⁻⁹⁺), 107.8 (C₋¹⁰⁻), 70.6 (C⁻¹¹⁻), 69.8 (C⁻¹²⁻), 67.9 (C⁻¹³⁻), 67.3 (C⁻¹⁴⁻). UV-Vis λ/nm (e/L mol⁻¹ cm⁻¹) (CH₂Cl₂, 1.00 × 10⁻⁵ mol L⁻¹) 237 (102 000), 280 (44 000), 312 (36 000), 325 (33 000), 350 sh (17 000), 400 sh (6000). ESI-MS m/z 1141.3 [M – PF₆⁻][base peak, calc. 1141.4]. Found C 57.75, H 4.61, N 4.56; C₄₅H₃₂F₂Ir₂N₄O₆P requires C 57.89, H 4.07, N 4.36%.
The method was as for [Ir(1)(2)][PF$_6$] starting with [Ir(1)(MeOH)][PF$_6$] (100 mg, 0.096 mmol), and NH$_4$PF$_6$ (156 mg, 0.960 mmol) in MeOH (20 mL). Column chromatography used silica eluting with CH$_2$Cl$_2$:MeOH 100:0.5 and finally CH$_2$Cl$_2$:MeOH 100:1. [Ir(1)(2)][PF$_6$] was isolated as an orange solid (101 mg, 0.072 mmol, 75.0%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$) δ ppm 8.15–8.07 (overlapping m, 4H, H$_{66}$), 7.69 (dd, $J = 8.4$, 7.5, 1.5 Hz, 2H, H$_B^4$), 7.67 (dd, $J = 8.6$ Hz, 2H, H$_N^4$), 7.32 (dd, $J = 8.1$ Hz, 2H, H$_{63}$), 7.25 (d, $J = 2.0$ Hz, 2H, H$_E^5$) 7.00 (dd, $J = 7.3$, 1.3 Hz, 2H, H$_E^5$), 6.98–6.91 (overlapping m, 6H, H$_{E4+N1+N5}$), 6.77–6.69 (overlapping m, 6H, H$_A^3$), 6.58 (br, 4H, H$_B^2$), 6.00 (dd, $J = 8.6$, 2.5 Hz, 2H, H$_A^4$), 4.65 (dd, $J = 2.5$, 2H, H$_B^4$), 4.08–3.96 (m, 4H, H$_A^4$), 3.80–3.74 (m, 2H, H$_D^4$), 3.69–3.63 (m, 2H, H$_B^b$), 3.59–3.53 (m, 2H, H$_D^d$), 3.53–3.45 (m, 4H, H$_T$), 1.40 (s, 18H, H$_{tBu}$-ring E). 13C NMR (126 MHz, CD$_2$Cl$_2$) δ ppm 168.1 (CB$_2$), 165.3 (CE$_6$), 164.7 (CE$_4$), 160.0 (CE$_2$), 159.2 (CA$_5$), 157.9 (CN$_2$), 150.2 (C$_B^6$), 149.5 (C$_A^1$), 138.5 (C$_G^1$), 138.2 (B$_F^3$), 136.4 (C$_B^A_3$), 129.3 (C$_N^4$), 128.8 (C$_S^2$), 128.0 (C$_S^2$), 127.8 (C$_N^2$), 126.8 (C$_N^2$), 126.0 (C$_A^1$), 124.9 (C$_N^4$), 121.6 (C$_E^5$), 121.0 (C$_A^4$), 118.8 (C$_B^6$), 117.3 (C$_N^3$), 116.2 (C$_A^6$), 109.2 (C$_N^1$), 107.8 (C$_N^1$), 70.6 (C$_C^6$), 69.8 (C$_C^6$), 67.9 (C$_C^6$), 67.3 (C$_C^6$), 36.0 (C$_{quat-Bu}^B$), 30.5 (C$_{quat-Bu}^B$). UV-Vis $\lambda$/nm (e/L mol$^{-1}$ cm$^{-1}$) (CH$_2$Cl$_2$), 1.00 × 10$^{-5}$ mol L$^{-1}$) 236 (107 000), 280 (52 000), 311 (37 000), 326 (28 000), 350 sh (16 000), 400 sh (7000). ESI-MS m/z 1177.4 [M – PF$_6$]$^-$ (base peak, calc. 1177.5). Found C 58.52, H 5.25, N 4.58; C$_{64}$H$_{64}$F$_6$IrN$_4$O$_6$P requires C 58.13, H 4.88, N 4.24%.}

Computational details

Dispersion-corrected density functional calculations (DFT-D) were carried out with the D.01 revision of the Gaussian 09 program package.$^{24}$ The Becke’s three-parameter B3LYP exchange–correlation functional$^{25,26}$ was used, together with the 6-31G** basis set for C, H, N and O, and the “double-ζ” quality LANL2DZ basis set for Ir. Intramolecular non-covalent interactions are expected to play a relevant role in the studied systems. Consequently, to get a better description of their molecular geometry, the Grimmed D3 dispersion term with Becke-Johnson damping was added to the B3LYP functional (B3LYP-D3).$^{29,30}$ The geometries of both the singlet ground electronic state (S$_0$) and the lowest-energy triplet state (T$_1$) were fully optimized. No symmetry restrictions were imposed. The geometry of T$_1$ was calculated at the spin-unrestricted UB3LYP-D3 level using a spin multiplicity of three. All the calculations were performed in the presence of the solvent (CH$_2$Cl$_2$). Solvent effects were considered within the self-consistent reaction field (SCRF) theory using the polarized continuum model (PCM) approach.$^{31–33}$ Time-dependent DFT (TD-DFT)$^{14–16}$ calculations of the lowest-lying 30 singlet excited states and the lowest-lying 10triplets of all the complexes were performed in the presence of the solvent at the minimum-energy geometry optimized for the ground state. The geometry of the first naphthyl-centred triplet excited state of each system was first optimized at TD-DFT level, and then reoptimized at the UB3LYP-D3 level to compare with the results obtained for T$_1$ from DFT calculations.

Device preparation

LEC devices were prepared on top of a patterned indium tin oxide (ITO, 15 Ω per square) coated glass substrate (http://www.naranjosubstrates.com) previously cleaned as follows: (a) sonication with soap, (b) deionized water, (c) isopropanol and (d) UV-O$_3$ 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, 80 nm 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 increase the reproducibility of the cells. The emitting layer (100 nm) was prepared by spin-coating of a MeCN 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). The devices were then transferred to an inert atmosphere glovebox (<0.1 ppm O₂ and H₂O, MBraun), where 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 and the luminance versus time by a True Colour Sensor MAZeT (MTCSiCT Sensor) with a Botest OLT OLED Lifetime-Test System. The average current density is determined by multiplying the peak current density by the time-on time and dividing by the total cycle time. The average luminance is directly obtained by taking the average of the obtained photodiode results and correlating it to the value of a luminance meter. The current efficiency is obtained by dividing the average luminance by the average current density. The electroluminescent (EL) spectra were measured using an Avantes AvaSpec-2048 Fiber Optic Spectrometer during device lifetime measurement.

**Results and discussion**

**Synthesis and characterization of ligand H₂ and solvento precursor [Ir(1)(MeOH)₂][PF₆]**

Scheme 1 summarises the synthetic route to the bis(cyclometallating) ligand H₂. The precursor 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene was prepared following published procedures. The choice of 2-(4-fluorophenyl)pyridine as substrate and the reaction conditions for nucleophilic substitution with 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene were chosen based on those described by Clavier *et al.* for the formation of 8-(tert-butylthio)-2-methylquinoline. Compound H₂ was isolated in 74.6% yield. The base peak in the electrospray mass spectrum (m/z 643.6) arose from the [M + H]⁺ ion, and elemental analysis was in accord with the expected composition. The ¹H and ¹³C NMR spectra were assigned by 2D methods (COSY, NOESY, HMQC and HMBC) and the spectra were consistent with the symmetrical structure shown in Scheme 1 for H₂.

The conventional methodology for preparing complexes of the type [Ir(C’N₂)(N’N)][PF₆] is treatment of a [Ir(C’N₂)(µ-Cl)]₂ dimer with two equivalents of an N’N ligand followed by anion exchange. However, the unfavourable effect that residual chloride ion has on the performance of LEC devices has led us to develop an alternative strategy in which the chlorido dimer is converted to an intermediate solvento complex by treatment of the dimer with AgPF₆ in methanol (Scheme 2). The dimer [Ir₂(1)(µ-Cl)]₂ was prepared from H₂ and IrCl₃·xH₂O under dilute conditions to ensure that the two C’N coordination sites of H₂ underwent cyclometallation at the same iridium(m) centre. The dimer was then treated with AgPF₆ in MeOH to give the solvento complex [Ir(1)(MeOH)]₂[PF₆] which was used for the final reaction step without further purification. Both [Ir₂(1)(µ-Cl)]₂ and [Ir(1)(MeOH)]₂[PF₆] were characterized by ESI MS and NMR spectroscopy. The base peak envelope in the mass spectrum of each complex corresponded to the [Ir(1)]⁺ cation. Evidence for the coordinated MeOH in [Ir(1)(MeOH)]₂[PF₆] came from δ(¹H) and δ(¹³C) NMR signals at 3.34 and 49.9 ppm, respectively. These values compare with δ(¹H) = 3.35 ppm and δ(¹³C) = 49.9 ppm in [Ir(Phppy)(MeOH)]₂[PF₆] and [Ir(Ph₂ppy)(MeOH)]₂[PF₆] (HPhppy = 2-(3-phenyl)phenylpyridine and HPh₂ppy = 2-(3,5-diphenyl)phenylpyridine). Going from H₂ to the coordinated ligand in [Ir₂(1)(µ-Cl)]₂ and [Ir(1)(MeOH)]₂[PF₆] results in a loss in rotational freedom within the polyethyleneoxy-chain, with the consequence that each

![Scheme 1](image1.png)

**Scheme 1** Synthesis of [Ir(1)(MeOH)]₂[PF₆] and [Ir(C’N₂)(N’N)][PF₆] salts. Conditions: (i) AgPF₆, MeOH; (ii) ligand 2, 3, 4 or 5, NH₄PF₆, MeOH, reflux 20 h. Atom labelling for NMR assignments is given: for C₂ symmetric complexes, a = e, b = f, etc., ring A = C, ring B = D, and ring E = F; phenyl substituent = ring G.
pair of CH₃ protons appears as a diastereotopic pair (see Experimental section and discussion of the [Ir(1)(N′N)]⁺ complexes).

**Synthesis and characterization of [Ir(1)(N′N)][PF₆] complexes**

The complexes [Ir(1)(N′N)][PF₆] with N′N = 2, 3, 4 or 5 were prepared by reaction of [Ir(1)(MeOH)]₂[PF₆] with the N′N ligand in MeOH at reflux in the presence of NH₄PF₆ (Scheme 2). After work up, [Ir(1)(2)][PF₆], [Ir(1)(3)][PF₆], [Ir(1)(4)][PF₆] and [Ir(1)(5)][PF₆] were isolated in 44.1–75.0% yields. The base peak in the electrospray mass spectrum of each compound corresponded to [M − PF₆]⁺ and the isotope pattern of the peak envelope was as predicted. The ¹H and ¹³C NMR spectra of the complexes were assigned by using COSY, NOESY, HMQC and HMBE experiments. The cations [Ir(1)(2)]⁺ and [Ir(1)(4)]⁺ are C₂ symmetric and Fig. 2 shows the solution ¹H NMR spectrum of [Ir(1)(2)][PF₆]. The change in the appearance of the alkyl signals on going from H₄A (Fig. 1) to [Ir(1)(2)][PF₆] (Fig. 2) is consistent with each CH₂ group in the coordinated ligand exhibiting a diastereotopic pair of protons. The ¹H NMR spectrum of [Ir(1)(4)][PF₆] is similar to that of [Ir(1)(2)][PF₆], but with the absence of the signal for H₄D and the addition of a singlet at δ 1.40 ppm arising from the tertBu substituent in ligand 4. The low frequency shift of the signal for H₄D (δ = 4.62 ppm in [Ir(1)(2)][PF₆]) and δ = 4.65 ppm in [Ir(1)(4)][PF₆] is due to a combination of H₄D being sandwiched in a V-shaped cavity between a phenyl and pyridine ring (as observed in related [Ir(C≡N)(N′N)]⁺ complexes and from its proximity to one or more oxygen atoms of the polyethyleneoxy-chain. Unfortunately, no X-ray quality single crystals of any of the four complexes could be grown. In Fig. 2, the broadened signal at δ 6.55 ppm for protons H₄G (the ortho-protons on the 6- and 6′-phenyl substituents of ligand 2) is consistent with hindered rotation of the phenyl rings as observed in other [Ir(C≡N)(N′N)⁺] complexes with 6-phenyl-2,2′-bipyridine or 6,6’-diphenyl-2,2′-bipyridine N′N ligands. A similarly broadened resonance for HG₂ appears at δ 6.58 ppm in the ¹H NMR spectrum of [Ir(1)(4)][PF₆].

On going from [Ir(1)(2)]⁺ and [Ir(1)(4)]⁺ to [Ir(1)(3)]⁺ and [Ir(1)(5)]⁺, the complex is desymmetrized. This is apparent from the ¹H NMR spectrum for [Ir(1)(3)][PF₆] (Fig. 3) compared to that of [Ir(1)(2)][PF₆] (Fig. 2). Signals for both H₄G (δ = 6.57 ppm) and H₄D (δ = 6.76 ppm) are broadened in the ¹H NMR spectrum of [Ir(1)(3)][PF₆] (Fig. 3), and similarly broadened signals are observed for H₄G (δ = 6.58 ppm) and H₄D (δ = 6.76 ppm) in [Ir(1)(5)][PF₆]. As in [Ir(1)(2)][PF₆] and [Ir(1)(4)][PF₆], this indicates hindered rotation of the 6-phenyl substituent.

**Electrochemistry**

The electrochemical behaviour of the [Ir(1)(N′N)][PF₆] complexes was investigated using cyclic voltammetry and data are shown in Table 1. A representative cyclic voltammogram (CV) is depicted in Fig. 4. Each complex exhibits an irreversible oxidation and a quasi-reversible reduction process, which are compared to the reference compound [Ir(ppy)₃][PF₆] (Hppy = 2-phenylpyridine). The value of Eox is only marginally affected by the introduction of electron-releasing phenyl and/or tert-butyl groups on the ancillary ligands (e.g. from +0.80 to +0.76 V on going from [Ir(1)(3)][PF₆] to [Ir(1)(4)][PF₆]), leading to a slightly destabilized HOMO. These findings are consistent with the oxidation process being centred on the iridium and C≡N ligand, as discussed previously.

The reduction processes centred on the N′N ligand are similar for [Ir(1)(4)][PF₆] and [Ir(1)(5)][PF₆] (−1.96 V and...
Photophysical properties

The solution absorption spectra of [Ir(1)(N’-N’)][PF$_6$] complexes and reference compound [Ir(ppy)$_2$] in CH$_2$Cl$_2$ (1.00 × 10$^{-5}$ mol L$^{-1}$) are shown in Fig. 5. On going from [Ir(1)(3)][PF$_6$] to [Ir(1)(5)][PF$_6$], the electron-releasing tert-butyl groups are introduced into the N’N domain and there is a significant shift of $E_{1/2}^{\text{red}}$ to more negative potentials. This is consistent with the LUMO of the complex being localized on the N’N ligand as discussed below and in agreement with, for example, [Ir(ppy)$_2$(2)][PF$_6$].

$\Delta E_{1/2} = -1.92$ V, respectively) compared to $-1.94$ V for [Ir(ppy)$_2$(4)][PF$_6$]. On going from [Ir(1)(2)][PF$_6$] to [Ir(1)(4)][PF$_6$] and from [Ir(1)(3)][PF$_6$] to [Ir(1)(5)][PF$_6$], electron-releasing tert-butyl groups are introduced into the N’N domain and there is a significant shift of $E_{1/2}^{\text{red}}$ to more negative potentials. This is consistent with the LUMO of the complex being localized on the N’N ligand as discussed below and in agreement with, for example, [Ir(ppy)$_2$(2)][PF$_6$].

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−1.92 V, respectively) compared to $-1.94$ V for [Ir(ppy)$_2$(4)][PF$_6$]. On going from [Ir(1)(2)][PF$_6$] to [Ir(1)(4)][PF$_6$] and from [Ir(1)(3)][PF$_6$] to [Ir(1)(5)][PF$_6$], electron-releasing tert-butyl groups are introduced into the N’N domain and there is a significant shift of $E_{1/2}^{\text{red}}$ to more negative potentials. This is consistent with the LUMO of the complex being localized on the N’N ligand as discussed below and in agreement with, for example, [Ir(ppy)$_2$(2)][PF$_6$].
Table 2 Emission maxima and quantum yields for [Ir(1)(N^N)][PF_6] complexes in solution and as powder samples

<table>
<thead>
<tr>
<th>Complex cation</th>
<th>CH_2Cl_2 solution</th>
<th>Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(1)(2)][PF_6]</td>
<td>434, 590</td>
<td>16</td>
</tr>
<tr>
<td>[Ir(1)(3)][PF_6]</td>
<td>361, 601</td>
<td>6</td>
</tr>
<tr>
<td>[Ir(1)(4)][PF_6]</td>
<td>425, 564</td>
<td>9</td>
</tr>
<tr>
<td>[Ir(1)(5)][PF_6]</td>
<td>435, 578</td>
<td>18</td>
</tr>
<tr>
<td>[Ir(ppy)(4)][PF_6]</td>
<td>420, 558</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ \lambda_{	ext{exc}} = 280 \text{ nm.} \] \[ \text{Argon degassed.} \] \[ A \text{ value of 555 nm has been reported for a CH_2Cl_2 solution of [Ir(ppy)(4)][PF_6].} \]

The emission spectra of the [Ir(1)(N^N)][PF_6] complexes as amorphous thin films with the composition used in LEC devices were also recorded (Fig. S1). The spectra are similar and follow the same trends discussed above for the powder complexes with the emission maxima slightly red-shifted (Ir(1)(2))[PF_6]: 583 nm, [Ir(1)(3)][PF_6]: 589 nm, [Ir(1)(4)][PF_6]: 574 nm, [Ir(1)(5)][PF_6]: 579 nm). The PLQY values (see Table 4) obtained in thin film are comparable to those determined in powder (21.9% for [Ir(1)(5)][PF_6], 17.5% for [Ir(1)(4)][PF_6] and 15.5% for [Ir(1)(3)][PF_6]) except for [Ir(1)(2)][PF_6] which shows a significantly lower PLQY of 22.6% compared to 35% in the powder (Table 2).

A comparison of Fig. 6 and 7 reveals that each complex in solution, most noticeably [Ir(1)(4)][PF_6], exhibits a second emission at higher energies than the dominant band, and that this emission band is absent in the powder samples. Since the aim of introducing the naphthyl domain into the [Ir(C^N)2(N^N)]\(^+\) complex was to generate a dual emitter, the appearance of the second band, albeit weak, demanded further investigation. The absence of the band in the solid state samples suggested that the high-energy emission might arise from dissociated ligand. Fig. 8 shows an overlay of the normalized emission spectra of [Ir(1)(4)][PF_6], [Ir(ppy)(4)][PF_6], H_21 and 4. Both [Ir(1)(4)][PF_6] and [Ir(ppy)(4)][PF_6] exhibit a band with \(\lambda_{\text{em}}\sim 420 \text{ nm} \) (Table 2), suggesting that the origin of the emission is not the naphthyl domain. Note that the previously reported emission spectrum of [Ir(ppy)(4)][PF_6] did not extend to below 450 nm. Model compounds HOnaphth (HOnaphth = 2,7-bis[2-(2-hydroxyethoxy)ethoxy]naphthalene) and H_21 both show a structured emission at 331 and 344 nm typical of naphthalene; in addition, [Ir(ppy)(4)][PF_6] and [Ir(ppy)(4)][PF_6] exhibit an emission at 410 nm. Unexpectedly, excitation of a CH_2Cl_2 solution of ligand 4 gives rise to an extremely similar PL spectrum as that of H_21 and HOnaphth (Fig. 8). Repeated measurements for 4 and comparisons with the emission spectrum of 5 and with the reported emission spectrum of 4,4′-di-tert-butyl-2,2′-bipyridine (\(\lambda_{\text{em}}\) = 357 nm) validated the result.

Excitation spectra of [Ir(1)(4)][PF_6] and [Ir(ppy)(4)][PF_6] (Fig. S2) reveal the origins of the 564 and 425 nm emissions in [Ir(1)(4)][PF_6] and the 558 and 420 nm bands in [Ir(ppy)(4)][PF_6]. The low-energy MLCT emissions for both complexes arise from absorptions over the whole region from 230 to 500 nm, and the profiles of the excitation spectra are

Table 3 Emission lifetimes for [Ir(1)(N^N)][PF_6] complexes in solution and as powder samples

<table>
<thead>
<tr>
<th>Complex cation</th>
<th>CH_2Cl_2 solution</th>
<th>Powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(1)(2)][PF_6]</td>
<td>587</td>
<td>381</td>
</tr>
<tr>
<td>[Ir(1)(3)][PF_6]</td>
<td>601</td>
<td>159</td>
</tr>
<tr>
<td>[Ir(1)(4)][PF_6]</td>
<td>564</td>
<td>144</td>
</tr>
<tr>
<td>[Ir(1)(5)][PF_6]</td>
<td>420</td>
<td>4</td>
</tr>
<tr>
<td>[Ir(ppy)(4)][PF_6]</td>
<td>579</td>
<td>365</td>
</tr>
</tbody>
</table>

\[ \text{Bi-exponential fit using the equation} \]

\[ \tau = \sum A_i \tau_i \]

\[ A_i \text{ is the pre-exponential factor of the lifetime.} \]
similar to the absorption spectra shown in Fig. 5, but, as expected, lack the naphthyl band at 237 nm. The 425 or 420 nm emission results from two absorption bands at ~258 and ~358 nm (Fig. 9, black and cyan spectra). The excitation spectra for [Ir(1)(4)]PF$_6$ and [Ir(ppy)$_2$(4)]PF$_6$ resemble that of 4 (Fig. 9). In contrast, the excitation spectrum of H$_2$1 for the emission at 410 nm (Fig. 9, green spectrum) is broader. The similarity between the excitation spectra of [Ir(1)(4)]PF$_6$, [Ir(ppy)$_2$(4)]PF$_6$ and free ligand 4 indicate that the high-energy emission around 420 nm arises from a fluorescent excited state of coordinated ligand 4. Although an extremely low concentration impurity could be responsible for such observations, the method of measuring and the reproducibility of recorded solutions of independently synthesized compounds makes this scenario unlikely.

The PLQY increases from 1% to 9% on going from [Ir(ppy)$_2$(4)]PF$_6$ to [Ir(1)(4)]PF$_6$, but this is not necessarily a consequence of partial energy transfer from the naphthyl unit (PLQY = 15% for H$_2$1) to the Ir(III) coordination sphere. Excited-state lifetime measurements of [Ir(1)(4)]PF$_6$ ($\tau_{av}$ = 144 ns for the 564 nm and $\tau_{av}$ = 4 ns for the 420 nm emission band, Table 3) corroborate the fact that the higher-energy emission arises from a fluorescent excited state being in the same range as for H$_2$1 ($\tau_{av}$ = 6 ns for the 420 nm emission band).

**Theoretical calculations**

To gain a better understanding of the electrochemical and photophysical properties of complexes [Ir(N^N)N]$_2$ (N^N = 2–5), a combined DFT/TD-DFT theoretical investigation was undertaken at the B3LYP-D3/(6-31G** + LANL2DZ) level in the presence of the solvent (CH$_2$Cl$_2$) (see the Experimental section for full computational details). Calculations were also performed for the reference complex [Ir(ppy)$_2$(4)]$^+$ for comparison purposes.

The geometry of the complexes in their ground electronic state ($S_0$) was optimized without imposing any symmetry restriction. The calculated geometries reproduce the trends observed typically on this type of complexes, showing a distorted octahedral coordination of the iridium atom. Fig. 10 displays the minimum-energy optimized structures of complexes [Ir(1)(2)]$^+$ and [Ir(1)(3)]$^+$ as representative examples. Table S1† summarizes the values of the geometrical parameters defining the iridium coordination sphere and of selected distances and dihedral angles. For all the complexes, the pendant phenyl rings introduced as R and R$_1$ substituents in the N^N ligand (Scheme 2) present intracation face-to-face π-stacking interactions with the phenyl rings of the closest ppy in the cyclometallating ligand. The calculated centroid–centroid distances between rings A and G in Scheme 2 range from 3.40 to 3.56 Å, in good agreement with the X-ray values reported for complexes [Ir(ppy)$_2$(2)]$^+$ and [Ir(ppy)$_2$(3)]$^+$. The steric hindrance produced by the phenyl substituents induces a twisting between the rings of the bpy ligand. The twisting angle is higher for [Ir(1)(2)]$^+$ (32.8°), [Ir(1)(4)]$^+$ (38.3°) and [Ir(ppy)$_2$(4)]$^+$ (37.1°) than for [Ir(1)(3)]$^+$ (21.3°) and [Ir(1)(5)]$^+$.
(24.9°) because in the former two pendant phenyl rings are introduced in R and R1 positions. For all the [Ir(1)2(N=N)] complexes, the cyclometallating ligand 1 remains in an expanded disposition (Fig. 10), featuring a distance from the centroid of the naphthalene group to the iridium atom of 10.6–10.8 Å.

The geometry of the complexes in their first triplet excited state (T1) was also optimized using the spin-unrestricted UB3LYP-D3/6-31G**+LANL2DZ approach. It is worth to note that the face-to-face intracation interactions observed in the ground state are preserved in T1, and that the naphthalene-iridium distance remains almost constant. The most important changes are found for the bpy ligand that becomes more planar in T1 (twisting angles in the 13–18° range, Table S1, ESIF). This points to a higher electron density on the bpy ligand in T1, which would stabilize the planar form as it favors the electronic delocalization.

Fig. 11 displays the isovalue contours calculated for the highest-occupied (HOMO) and lowest-unoccupied (LUMO) molecular orbitals of complex [Ir(1)(2)] as a representative example. Orbitals HOMO−1 and LUMO+7, which respectively correspond to the highest-occupied and lowest-unoccupied molecular orbitals centred on the naphthalene group of ligand 1, are also displayed. The topology of the corresponding MOs of all the [Ir(1)(N=N)] complexes fully reproduces that of the selected example. The table inserted in Fig. 11 summarizes the MO energies calculated for the [Ir(1)(N=N)] complexes and compares them with those obtained for the HOMO and LUMO of [Ir(pppy)2(4)] . As it is usually found for ppy-based cyclometallated Ir-iTMCs, the HOMO results from a mixture of dπ orbitals of Ir(III) and phenyl π orbitals, with some contribution from the pyridine rings, of the cyclometallating ligand, whereas the LUMO is located over the bpy of the ancillary ligand. The similar energy values estimated for the HOMO of [Ir(1)(N=N)] are in good agreement with the experimental  E_{ox} values (Table 1), which do not change greatly along the series.

The introduction of electron-releasing tert-butyl groups in the N=N ligand slightly destabilizes the HOMO of [Ir(1)(4)] and [Ir(1)(5)], in good agreement with the slightly lower E_{ox} recorded for these complexes. The effect of the substituents is higher in the LUMO, centred on the ancillary ligand. It becomes stabilized along the series [Ir(1)(4)] (−2.30 eV) > [Ir(pppy)2(4)] (−2.34 eV) > [Ir(1)(5)] (−2.41 eV) > [Ir(1)(2)] (−2.47 eV) > [Ir(1)(3)] (−2.56 eV), in quite good correlation with the less negative E_{red} values recorded along this series (Table 1).

The HOMO–LUMO gaps calculated for [Ir(1)(2)] (3.20 eV) and [Ir(1)(3)] (3.13 eV) are lower than those computed for [Ir(1)(4)] (3.33 eV) and [Ir(1)(5)] (3.24 eV) in good accord with the trends observed for the electrochemical gap ΔE_{1/2}. If light emission in these complexes originates from a state described by the HOMO → LUMO excitation, MO calculations predict that [Ir(1)(4)] would emit more in the blue that the rest of the complexes and close to the emission of [Ir(pppy)2(4)]. This is in fact the trend observed in solution for the  Emax values (Table 2). The significant energy difference between the LUMO and the LUMO+7 centred on the naphthalene moiety leads us to expect that states associated to this moiety will appear at high energies and will not contribute to the emission.

The nature of the low-lying triplet states was first studied by performing TD-DFT calculations at the optimized geometry of the ground state (S0). The vertical excitation energies and electronic descriptions computed for the lowest-lying triplet states of the [Ir(1)(N=N)] complexes and those of [Ir(pppy)2(4)] are given in Table S2. All the complexes present a first triplet excited state (T1) mainly defined by the HOMO → LUMO excitation, which implies an electron transfer from the Ir-ppy environment, where the HOMO is localized, to the bpy ligand, where the LUMO resides (see Fig. 11). The T1 state therefore shows a mixed 3MLCT/3LLCT character, and the calculated excitation energies ([Ir(pppy)2(4)]: 2.56 eV > [Ir(1)(4)]: 2.55 eV > [Ir(1)(5)]: 2.53 eV > [Ir(1)(2)]: 2.48 eV > [Ir(1)(3)]: 2.43 eV) follow the trend expected on the basis of the HOMO–LUMO gap. The T1 state was further examined by optimizing its structure at the spin-unrestricted UB3LYP-D3 level as described above. The unpaired-electron spin density distribution calculated for this state (Fig. 12a) matches the topology of the HOMO → LUMO excitation and therefore corroborates the electron transfer from the Ir-ppy environment to the N=N ligand, thus confirming the 3MLCT/3LLCT character of T1. The electronic nature predicted for T1 is in good agreement with the broad unstructured shape of the emission bands observed experimentally (Fig. 6 and 7).

Back to the TD-DFT calculation of triplet states, the first excited state involving the naphthyl group of ligand 1 is found 0.3–0.4 eV above T1 (Table S2†). As was to be expected, it is mainly described by the HOMO → 1 LUMO excitation, and its vertical excitation energy from S0 remains almost constant (2.85–2.86 eV) for all the [Ir(1)(N=N)] complexes, as the structural differences between these complexes concern the N=N ligand from which the naphthyl is far apart. The spin-density distribution calculated for this state is shown in Fig. 12b and clearly reflects the localization of the electronic transition on
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From now on, LECs containing [Ir(iTMC)]4+ were investigated by incorporating them as emitters in LECs. This journal is © The Royal Society of Chemistry 2016

Time to reach the maximum luminance

Table 4 Performance of ITO/PEDOT:PSS/active layer/Al LECs measured using a pulsed current driving (average current density 25 A m⁻², 1000 Hz, 50% duty cycle). Active layer = Ir-iTMC : [Bmim][PF₆] 4 : 1 molar ratio

<table>
<thead>
<tr>
<th>LEC</th>
<th>Ir-iTMC</th>
<th>Lmax /h</th>
<th>Lmax /cd m⁻²</th>
<th>t₁/₂ /h</th>
<th>Efficacy /cd A⁻¹</th>
<th>PCE /%</th>
<th>EQE /%</th>
<th>PLQY /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>[Ir(1)(2)][PF₆]</td>
<td>48.6</td>
<td>91</td>
<td>785</td>
<td>4.2</td>
<td>2.1</td>
<td>1.8</td>
<td>22.6</td>
</tr>
<tr>
<td>B</td>
<td>[Ir(1)(3)][PF₆]</td>
<td>52.1</td>
<td>67</td>
<td>581</td>
<td>3.1</td>
<td>1.7</td>
<td>1.3</td>
<td>17.5</td>
</tr>
<tr>
<td>C</td>
<td>[Ir(1)(4)][PF₆]</td>
<td>61.8</td>
<td>54</td>
<td>626</td>
<td>2.5</td>
<td>1.3</td>
<td>0.8</td>
<td>15.5</td>
</tr>
<tr>
<td>D</td>
<td>[Ir(1)(5)][PF₆]</td>
<td>0.6</td>
<td>133</td>
<td>31</td>
<td>5.4</td>
<td>2.2</td>
<td>2.1</td>
<td>21.9</td>
</tr>
<tr>
<td>E</td>
<td>[Ir(ppy)(4)][PF₆]</td>
<td>3.3</td>
<td>146</td>
<td>26</td>
<td>6.4</td>
<td>3.7</td>
<td>2.6</td>
<td>—</td>
</tr>
</tbody>
</table>

a Time to reach the maximum luminance Lmax. b Time to reach one-half of the maximum luminance. c Maximum efficacy. d Maximum power conversion efficiency. e Maximum external quantum efficiency. f Photoluminescence quantum yield in thin film using the same composition than for the device active layer (λexc = 320 nm).
device performances. The turn-on time \( t_{\text{max}} \) is defined as the time to reach the maximum luminance \( L_{\text{max}} \) and the device lifetime \( t_{1/2} \) is the time to reach one-half of \( L_{\text{max}} \) after this value is achieved. LEC devices can be divided in two groups with LECs D and E, which incorporate complexes \([\text{Ir}(1)(5)][\text{PF}_6] \) and \([\text{Ir}(ppy)(4)][\text{PF}_6] \), showing shorter \( t_{\text{max}} \) and faster luminance decays than LECs A–C (Table 4). LECs D and E show \( t_{\text{max}} \) and \( t_{1/2} \) below 3.5 and 35 hours, respectively, whereas devices A–C have longer turn-on times above 45 hours and a much more stable behaviour with \( t_{1/2} \) values ranging from 581 to 785 hours. In contrast, LECs D and E achieve higher luminance values above 100 cd m\(^{-2} \) (133 and 146 cd m\(^{-2} \), respectively) compared with LECs A–C, which show maximum luminances of 91, 67 and 54 cd m\(^{-2} \), respectively. The maximum values obtained for the efficacy, the power conversion efficiency (PCE) and the external quantum efficiency (EQE) of LEC D (5.4 cd A\(^{-1} \), 2.2 lm W\(^{-1} \) and 2.1%, respectively), are slightly lower than those found for LEC E (6.4 cd A\(^{-1} \), 3.7 lm W\(^{-1} \) and 2.6%), and are similar to those reported for other orange-emitting Ir-TMC-LECUs under pulsed current operation.\(^{49,53} \) The efficiency, PCE and EQE values found for LECs A–C are smaller than those obtained for D, and decrease in passing from A to B and to C (Table 4). This trend is in agreement with the trend of the PLQY for the amorphous thin film (device environment) of the complexes \([\text{Ir}(1)(2)][\text{PF}_6], [\text{Ir}(1)(3)][\text{PF}_6] \) and \([\text{Ir}(1)(4)][\text{PF}_6] \).

The main differentiator between the complexes \([\text{Ir}(1)(5)][\text{PF}_6] \) and \([\text{Ir}(ppy)(4)][\text{PF}_6] \) used to prepare LECs D and E is the naphthyl-bridged functionalization of the ppy ligands in the case of LEC D. Yet both the device responses \( t_{\text{max}} \) and \( t_{1/2} \) are comparable for these two devices, which indicates that the ppy functionalization does not influence the ionic movement in the films. Therefore, the longer \( t_{\text{max}} \) and \( t_{1/2} \) found for LECs A–C should not be ascribed to the large size of ligand 1. Moreover, the \([\text{Ir}(1)(2)][\text{PF}_6] \) complex, used in the fabrication of LEC A, exhibits the highest PLQY in thin film (22.6%), whereas the device efficiency is superior for D incorporating a complex with a slightly lower PLQY (21.9%). Considering these PLQY values and a typical outcoupling of 20%, the theoretical maximum EQEs predicted for LECs A and D when all injected electrons and holes combine have very similar values of 4.5% and 4.4%, respectively. As the EQE achieved for D (2.1%) is slightly closer to the theoretical value than that obtained for A (1.8%), we can hypothesize that the lower exciton-quenching for D could be the result of a better-balanced carrier injection due to the faster response. Hence, for the devices with slower response (devices A–C), lower efficiencies were achieved. Comparable characteristics have been observed for similar orange complexes reported in LECs.\(^{41} \)

The electroluminescence (EL) spectrum of all the LECs was registered during the operation of the devices (Fig. S3†). All the LECs show orange electroluminescence with maxima in the 580–590 nm range but for LEC C \(([\text{Ir}(1)(4)][\text{PF}_6]) \) which emits at 575 nm. The EL spectra are similar to the PL spectra recorded in powder (Fig. 7) and in thin film (Fig. S1†).

Conclusions

We have prepared and characterized a series of cyclometallated \([\text{Ir}(C^\equiv N)\text{N}][\text{PF}_6] \) compounds in which the two cyclometallating C^\equiv N units are connected by a naphthyl-containing linker. The N^\equiv N ligand (2–5) is a 2,2’-bipyridine functionalized with phenyl and tert-butyl groups. The electrochemical and photophysical properties were compared with those of \([\text{Ir}(ppy)(4)][\text{PF}_6] \). The complexes containing the naphthyl-unit exhibit similar absorption spectra, which differ from that of \([\text{Ir}(ppy)(4)][\text{PF}_6] \) only in the presence of an intense absorption at \( \sim 236 \) nm arising from naphthyl-centred \( \pi \rightarrow \pi^* \) transitions. Excitation at 280 nm leads to an orange emission for solutions of each complex, and going from solution to powder or thin film leads to little change or to a small blue shift in the emission. The incorporation of the naphthalene unit does not lead to a desirable blue contribution to the emission, and DFT/ TD-DFT calculations were performed to understand this observation. The energy difference between the LUMO and the lowest-unoccupied MO centred on the naphthyl moiety (LUMO+7) is large enough to explain why there is no contribution from the naphthyl-centred triplet excited state to the phosphorescence emission. Singlet excited states were also investigated. LECs using the \([\text{Ir}(1)(N^\equiv N)][\text{PF}_6], \) \([\text{Ir}(ppy)(4)][\text{PF}_6] \) complexes in the emissive layer led to long living devices with modest turn-on times. The presence of the naphthyl-bridge between the cyclometallating units does not significantly alter the device response, indicating that it does not play a significant role in the ionic transport.

Acknowledgements

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Notes and references


