Near-UV to red-emitting charged bis-cyclometallated iridium(III) complexes for light-emitting electrochemical cells

Florian Kessler, Rubén D. Costa, Davide Di Censo, Rosario Scopelliti, Enrique Orti, Henk J. Bolink, Sebastian Meier, Wiebke Sarfert, Michael Grätzel, Md. Khaja Nazeeruddin and Etienne Baranoff

Received 18th April 2011, Accepted 8th September 2011
DOI: 10.1039/c1dt10698h

Herein we report a series of charged iridium complexes emitting from near-UV to red using carbene-based N:C ancillary ligands. Synthesis, photophysical and electrochemical properties of this series are described in detail together with X-ray crystal structures. Density Functional Theory calculations show that the emission originates from the cyclometallated main ligand, in contrast to commonly designed charged complexes using bidentate N:N ancillary ligands, where the emission originates from the ancillary N:N ligand. The radiative process of this series of compounds is characterized by relatively low photoluminescence quantum yields in solution that is ascribed to non-radiative deactivation of the excited state by thermally accessible metal-centered states. Despite the poor photophysical properties of this series of complexes in solution, electroluminescent emission from the bluish-green to orange region of the visible spectrum is obtained when they are used as active compounds in light-emitting electrochemical cells.

Introduction

Light-emitting electrochemical cells (LECs) based on ionic transition-metal complexes (iTMCs) are emerging as a promising alternative to organic light-emitting diodes (OLEDs). The major advantages of iTMC-based LECs over OLEDs originate from the use of solution processing and simpler architectures. Moreover, because of the presence of mobile ions under applied voltage, the ions migrate towards the electrodes and assist the charge injection in the device. Multi-layer architectures necessary in OLEDs for charge injection and transport are therefore not necessary in LECs. In addition, air-stable electrodes can be used which allows a non-rigorous encapsulation process. These characteristics make the industrial production of LECs promisingly easier. However, iTMCs-based LECs still present important drawbacks, which mainly concern the efficiency, the turn-on time and the white color emission. To achieve white-light emission in LECs, it is necessary to combine sky-blue and orange emitters in a two-component system or blue, green and red emitters in a three-component system. Stable and efficient orange LECs have been reported. Hence, the primary requirement for achieving white-light emission is to prepare ionic blue-emitting complexes. A few examples of blue emitters have been reported; however, their use in LECs has not provided high performances.

The typical kind of iTMCs used in LECs are charged bis-cyclometallated iridium(III) complexes which have attracted widespread interest in recent years due to their high phosphorescence quantum yield, relatively short radiative lifetime and wide color tunability. However, their reported emission wavelength is limited on the blue side of the visible spectrum to about 450 and 440 nm when bidentate and monodentate ancillary ligands are used, respectively. The use of bidentate ancillary ligands forming a five-membered ring with the central metal cation is advantageous over monodentates due to the improved stability provided by the chelation effect. The most common design of charged bis-cyclometallated iridium(III) complexes for LECs is based on a neutral N:N ancillary ligand such as bipyridine, phenanthroline, pyridine-pyrazole, pyridine-imidazole, pyridine-triazole and pyridine-tetrazole. Blue emission is obtained by introducing ancillary ligands with a higher-energy lowest-unoccupied molecular orbital (LUMO) than bipyridine, as emission originates from the ancillary ligand, and/or by stabilizing the highest-occupied molecular orbital (HOMO) through introduction of electron-withdrawing groups on the orthometallated phenyl ring.

In neutral iridium(III) complexes used in OLEDs, deep-blue emission has been achieved by using carbene-based ligands. In this manuscript we present a strategy based on a neutral...
pyridine-carbene (N'C) ancillary ligand forming a five-membered ring with the central iridium to prepare a series of charged bis-cyclometallated iridium complexes with emission ranging from near-UV to red. Based on experimental and theoretical data, we reasoned that due to the very high LUMO of the carbene ligand, the emission originates from the main cyclometallated ligand. This can be related to the case of non-chromophoric monodentate ancillary ligands. This design allows a straightforward tuning of the emission maximum of charged iridium(III) complexes using classical tuning strategies on the main C'N ligand. In particular this simple design allows deep-blue emission which is highly desirable for white emitting electroluminescent devices based on three components. LEC devices using some of these compounds as the primary active components show electroluminescence from bluish-green to orange.

Results and discussion

Synthesis

Since the first isolation of a stable N-heterocyclic carbene (NHC) in 1991, numerous stable NHCs have been prepared. In recent years, N-heterocyclic carbones have evolved into very powerful co-ligands for transition metal complexes. Usually the NHC ligand is introduced into the complexes as an entity starting from either free NHCs or suitable precursors. Another approach would be a stoichiometric transfer of carbene ligands from one metal to another (transmetalation). A wide range of transition metals has been used as the carbene donor; however, the most common metal for carbene transmetalations is silver. To follow this approach, we generated the silver-NHC complex in situ from its benzimidazolium precursor. The benzimidazolam iodide ancillary ligand was synthesized by a copper catalyzed N-arylation of benzimidazole with 2-bromo-4-methylpyridine followed by alkylation with methyl iodide.

Complexes 1–7 have been synthesized as depicted in Scheme 1. As reported in the literature, the chloro-bridged iridium dimer [Ir(C'N)2(m-Cl)]2 is easily accessible from commercially available IrCl3·3H2O and C'N ligand. Then, [Ir(C'N)2(μ-Cl)], the benzimidazolam ancillary ligand and Ag2O were dissolved in 1,2-dichloroethane under nitrogen and the mixture was refluxed overnight. After filtration through celite, the iodine salts of the complexes were extracted with aqueous KPF6 solution to generate the desired complexes as PF6 salts, which were further purified by column chromatography on silica and isolated in good to excellent yield (50–95%).

X-ray crystal structures

The X-ray crystal structures of complexes 2, 3, 4, 5 and 6 have been obtained from single crystals grown by slow diffusion of heptane into a dichloromethane solution of the complex (Fig. 1 and Table 1). All of them present similar structural parameters as seen in Table 2. They show a near-octahedral geometry with the two pyridines of the anionic cyclometallated ligands in trans position one to each other and the two orthometallated phenyl rings in cis position, retaining the geometry of the starting chloro-bridged iridium dimer. In all complexes the bite angle of the pyridine-carbene ancillary ligand is close to 76.5°, which is similar to the bite angle of a bipyridine ancillary ligand. While the iridium–carbon(carbene) distance (Ir–C1 in Table 2) is barely affected by the substitution on the C'N ligand and is about 2.07 Å for all complexes, the iridium–nitrogen(carbene) distance (Ir–N1 in Table 2) is more strongly affected and appears to shorten as the accepting capability of the phenyl in the trans position increases. Without substitution (complex 5), the Ir–N1 bond is 2.169(4) Å and shortens to 2.131(6) Å for complex 2. Finally, it should be noted that the length of the Ir–C3 bond is in all cases longer than the Ir–C2 bond, reflecting the strong trans-effect of the carbene group.
The oxidation potential of complex 5 (0.86 V) is similar to other [Ir(ppy)2(NN)]+ complexes (N-N = 2-(1H-pyrazol-1-yl)pyridine, Eox = 0.87 V; N-N = 1-phenyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole, Eox = 0.85 V; N-N = 2,2'-bipyridine, Eox = 0.86 V). As for 5, the oxidation potential for 4 (1.19 V) is almost the same as the other [Ir(2,4-difluoro-ppy)2(NN)]+ complexes (N-N = 2-(1H-pyrazol-1-yl)pyridine, Eox = 1.20 V; N-N = 1-phenyl-2-(pyridin-2-yl)-1H-benzo[d]imidazole, Eox = 1.19 V; N-N = pyridine-1,2,3-triazole derivatives, Eox = 1.19–1.26 V). This clearly indicates a similar HOMO localization on both the phenyl ring of the cyclometallated ligands and the iridium center. Indeed,
Table 3  Photophysical and electrochemical properties of complexes 1–7

<table>
<thead>
<tr>
<th></th>
<th>$E_{pa}$ (V) $^*$</th>
<th>$E_{pc}$ (V) $^*$</th>
<th>$\lambda_{em}$ (nm) (ε (10$^3$ M$^{-1}$ cm$^{-1}$))$^{a}$</th>
<th>$\lambda_{em}$ (nm)$^{b}$</th>
<th>$\tau$ (ns)$^{b}$</th>
<th>$\Phi_{em}$$^c$</th>
<th>$\lambda_{em}$ (nm), 77 K$^{d}$</th>
<th>$k_{r}$ (10$^5$ s$^{-1}$)</th>
<th>$k_{nr}$ (10$^6$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.20</td>
<td>–2.36i</td>
<td>242 (43.0) 274 (30.5) 333sh (2.60) 364sh (0.5) 400 (0.1) 425 (0.03)</td>
<td>435</td>
<td>8524</td>
<td>0.197</td>
<td>390</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>1.61</td>
<td>–2.20i</td>
<td>249 (64.0) 282 (37.7) 321 (14.2) 343sh (6.25) 400 (0.1) 425 (0.03)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>1.38</td>
<td>–2.06i</td>
<td>250 (72.1) 277 (54.3) 353sh (6.28) 411 (0.22) 435 (0.09)</td>
<td>447</td>
<td>647</td>
<td>0.083</td>
<td>[106]</td>
<td>443</td>
<td>1.28</td>
</tr>
<tr>
<td>4</td>
<td>1.19</td>
<td>–2.26</td>
<td>245 (61.3) 257sh (55.1) 281sh (36.4) 357 (5.73) 414 (0.25) 439 (0.09)</td>
<td>450</td>
<td>249</td>
<td>0.034</td>
<td>[202]</td>
<td>446</td>
<td>1.37</td>
</tr>
<tr>
<td>5</td>
<td>0.86</td>
<td>–2.43</td>
<td>251 (47.3) 266 (44.3) 306sh (18.5) 375 (5.11) 459 (0.11)</td>
<td>471</td>
<td>65</td>
<td>0.009</td>
<td>[199]</td>
<td>465</td>
<td>1.39</td>
</tr>
<tr>
<td>6</td>
<td>0.95</td>
<td>–1.81</td>
<td>251 (56.2) 273 (58.1) 325 (22.5) tail from 400 (5.84) to 509 (0.1)$^{e}$</td>
<td>588</td>
<td>155</td>
<td>0.057</td>
<td>[274]</td>
<td>537</td>
<td>3.68</td>
</tr>
<tr>
<td>7</td>
<td>0.71</td>
<td>–1.74</td>
<td>257 (88.5) 278sh (63.3) 326 (33.2) 417 (12.8) 464 (7.18) 610sh (0.05)</td>
<td>663</td>
<td>1569</td>
<td>0.061</td>
<td>[1615]</td>
<td>635</td>
<td>0.39</td>
</tr>
</tbody>
</table>

$^*$ From CV measurements, $E = 1/2(E_{pa}+E_{pc})$; acetonitrile/TBAPF$_6$ 0.1 M, vs. Fc$^+/Fc$; $i$ denotes an irreversible potential. $^a$ Acetonitrile at room-temperature. $^b$ Contains several poorly-resolved shoulders. $^c$ Degassed acetonitrile at room temperature; $\tau$: lifetime of excited state; $\Phi_{em}$: photoluminescence quantum yield in solution. $^d$ Tetrahydrofuran. $^e$ Calculated using the relations $k_r = \Phi_{em}/\tau$ and $k_{nr} = 1/\tau - k_r$.

Fig. 2  CVs of complexes 3 (red line), 5 (blue line) and 7 (black line), scan rate 1 V s$^{-1}$, 3rd scan.

This assumption is well supported by theoretical calculations (see below).

The redox potentials for charged iridium complexes containing one neutral N$^+$N ancillary ligand are usually practically independent of the substitution pattern of the cyclometallated ligand. However, in the case of this series of complexes, despite having identical ancillary ligands, the reduction potentials are significantly different from one complex to another. These differences are attributed to different substitution patterns on the cyclometallated main ligand. The effect is especially marked for complexes 6 (~1.81 V) and 7 (~1.74 V) compared to complex 5 (~2.43 V). For complexes 2, 3 and 4, the electron withdrawing groups on the cyclometallated phenyl affect the reduction potentials as well, as they are stabilized compared to 5. Finally, the reversibilities of the electrochemical processes differ significantly going from one complex to another as seen in Fig. 2. All this strongly points to the electroactive LUMOs being localized at least partly on the main ligand, in contrast to complexes having an N$^+$N ancillary ligand.

Photophysical properties

UV-visible absorption spectra measured in acetonitrile solution at room temperature (Table 3 and Fig. 3) display strong bands in the UV up to 300 nm attributed to intraligand ($\pi$–$\pi^*$) transitions. Lower-energy absorption bands correspond to metal-to-ligand charge transfer (MLCT) transitions. Finally, weak bands with $\varepsilon \sim 100$ M$^{-1}$ cm$^{-1}$ are observed clearly for complexes 2, 3, 4 and 5 and poorly for 6 and 7. These bands are ascribed to spin-forbidden transitions directly to triplet states.

When excited at room temperature in the lowest energy $^1$MLCT band, the complexes show emission with low ($\Phi_{em} = 1\%$) to fair ($\Phi_{em} = 20\%$) photoluminescence quantum yield (Fig. 4 and Table 3). The exception is complex 1 which is non-emitting at room-temperature, as has been observed for the complex Ir(ppz)$_3$. This is additional support for the emission originating from the
main ligand and not from the ancillary ligand. Notably, 2 has the highest-energy emission maxima at 435 nm, significantly blue-shifted compared to commonly obtained blue emitters based on diimine ancillary ligands. While 2, 3, 4 and 5 exhibit structured emission spectra at room temperature, 6 and 7 show broad and unstructured emissions, pointing to a higher MLCT character in the excited state (S0) of those two complexes. When cooled to 77 K (Fig. 4), complex 1 emits at 390 nm, which is, to the best of our knowledge, the highest-energy-emitting charged iridium complex to date. To verify that this emission does not originate from an external source, the highest-energy-emitting charged iridium complex to date. To verify that this emission does not originate from an external source, excitation of the solvent under the same conditions has been performed to gain insight into the photophysical properties of the complexes. A particular interest was to gain support for the emission originating from the main ligand in contrast to charged iridium complexes having bidentate N_N ancillary ligands, where the emission originates from the ancillary ligand. Calculations have been limited to complexes 3, 4, 5 and 6 as representatives of the entire series.

The molecular structures of complexes 3–6 were investigated by performing DFT calculations at the B3LYP/6-31G**+LANL2DZ level (see the experimental section for details). The geometries of the complexes were fully optimized and show a similar near-octahedral coordination of the Ir metal to those observed in their X-ray structures. The Ir–C and Ir–N bond distances calculated for the four complexes in the electronic ground states (S0) are listed in Table 5 together with the experimental X-ray data. The structural trends remarked above from the experimental data are well supported by the theoretical calculations. For instance, the Ir–C1 distance remains constant (2.07 Å) for all complexes, slightly overestimating the experimental value (2.05 Å), and the Ir–C3 distance (~2.06 Å) is always longer than the Ir–C2 distance (~2.02 Å), likely due to the strong trans effect induced by the carbene group of the ancillary ligand. The Ir–N1 distance is also predicted to shorten upon the introduction of electron-withdrawing groups on the cyclometallated ligands, but the shortening calculated in passing from 5 to 3 (0.007 Å) is significantly less pronounced than that observed from X-ray data (0.020 Å). Notice that the calculated Ir–N and Ir–C(carbene) distances are overestimated, which is typically observed when using the B3LYP functional.

Table 4 Parameters used to calculate $k_r$ from Strickler–Berg equation (I)

<table>
<thead>
<tr>
<th>$\nu$ (cm$^{-1}$)</th>
<th>$\varepsilon_{\text{max}}$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$\Delta\nu^2_{\text{max}}$</th>
<th>$k_r$ calc. (10$^5$ s$^{-1}$)</th>
<th>$k_r$ exp. (10$^5$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23 640</td>
<td>34</td>
<td>974</td>
<td>0.32</td>
</tr>
<tr>
<td>3</td>
<td>22 989</td>
<td>84</td>
<td>928</td>
<td>0.71</td>
</tr>
<tr>
<td>4</td>
<td>22 779</td>
<td>87</td>
<td>910</td>
<td>0.73</td>
</tr>
<tr>
<td>5</td>
<td>21 786</td>
<td>109</td>
<td>840</td>
<td>0.76</td>
</tr>
<tr>
<td>6</td>
<td>20 576</td>
<td>644</td>
<td>910</td>
<td>4.29</td>
</tr>
<tr>
<td>7</td>
<td>16 369</td>
<td>51</td>
<td>878</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Theoretical calculations

Theoretical calculations on the ground and excited states were performed to gain insight into the photo- and electrochemical properties of the complexes. A particular interest was to gain support for the emission originating from the main ligand in contrast to charged iridium complexes having bidentate N_N ancillary ligands, where the emission originates from the ancillary ligand. Calculations have been limited to complexes 3, 4, 5 and 6 as representatives of the entire series.

The geometries of the complexes were fully optimized and show a similar near-octahedral coordination of the Ir metal to those observed in their X-ray structures. The Ir–C and Ir–N bond distances calculated for the four complexes in the electronic ground states (S0) are listed in Table 5 together with the experimental X-ray data. The structural trends remarked above from the experimental data are well supported by the theoretical calculations. For instance, the Ir–C1 distance remains constant (2.10 Å) for all complexes, slightly overestimating the experimental value (2.07 Å), and the Ir–C3 distance (~2.06 Å) is always longer than the Ir–C2 distance (~2.02 Å), likely due to the strong trans effect induced by the carbene group of the ancillary ligand. The Ir–N1 distance is also predicted to shorten upon the introduction of electron-withdrawing groups on the cyclometallated ligands, but the shortening calculated in passing from 5 to 3 (0.007 Å) is significantly less pronounced than that observed from X-ray data (0.020 Å). Notice that the calculated Ir–N and Ir–C(carbene) distances are overestimated, which is typically observed when using the B3LYP functional.
Table 5 Selected bond distances (in Å) calculated for complexes 3, 4, 5, and 6 in the S0 singlet ground state and in the T1 and the metal-centered (MC) triplet excited states. X-ray values are included for comparison.

<table>
<thead>
<tr>
<th>Exp. (Table 2)</th>
<th>S0</th>
<th>T1</th>
<th>3MC_Carbene</th>
<th>3MC_{ppy}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 Ir–N1</td>
<td>2.149(3)</td>
<td>2.226</td>
<td>2.231</td>
<td>2.216</td>
</tr>
<tr>
<td>Ir–N2</td>
<td>2.054(2)</td>
<td>2.082</td>
<td>2.064</td>
<td>2.075</td>
</tr>
<tr>
<td>Ir–N3</td>
<td>2.053(2)</td>
<td>2.091</td>
<td>2.097</td>
<td>2.080</td>
</tr>
<tr>
<td>Ir–C1</td>
<td>2.073(3)</td>
<td>2.100</td>
<td>2.112</td>
<td>2.097</td>
</tr>
<tr>
<td>Ir–C2</td>
<td>2.006(3)</td>
<td>2.017</td>
<td>2.002</td>
<td>2.046</td>
</tr>
<tr>
<td>Ir–C3</td>
<td>2.060(3)</td>
<td>2.061</td>
<td>2.058</td>
<td>2.045</td>
</tr>
<tr>
<td>4 Ir–N1</td>
<td>2.153(4)</td>
<td>2.227</td>
<td>2.232</td>
<td>2.223</td>
</tr>
<tr>
<td>Ir–N2</td>
<td>2.058(4)</td>
<td>2.081</td>
<td>2.099</td>
<td>2.083</td>
</tr>
<tr>
<td>Ir–N3</td>
<td>2.063(4)</td>
<td>2.090</td>
<td>2.067</td>
<td>2.072</td>
</tr>
<tr>
<td>Ir–C1</td>
<td>2.064(5)</td>
<td>2.101</td>
<td>2.107</td>
<td>2.103</td>
</tr>
<tr>
<td>Ir–C2</td>
<td>2.010(5)</td>
<td>2.022</td>
<td>2.004</td>
<td>2.045</td>
</tr>
<tr>
<td>Ir–C3</td>
<td>2.053(5)</td>
<td>2.064</td>
<td>2.062</td>
<td>2.050</td>
</tr>
<tr>
<td>5 Ir–N1</td>
<td>2.169(4)</td>
<td>2.233</td>
<td>2.249</td>
<td>2.252</td>
</tr>
<tr>
<td>Ir–N2</td>
<td>2.056(4)</td>
<td>2.083</td>
<td>2.104</td>
<td>2.081</td>
</tr>
<tr>
<td>Ir–N3</td>
<td>2.067(4)</td>
<td>2.091</td>
<td>2.074</td>
<td>2.073</td>
</tr>
<tr>
<td>Ir–C1</td>
<td>2.067(5)</td>
<td>2.100</td>
<td>2.115</td>
<td>2.093</td>
</tr>
<tr>
<td>Ir–C2</td>
<td>2.027(5)</td>
<td>2.025</td>
<td>1.984</td>
<td>2.046</td>
</tr>
<tr>
<td>Ir–C3</td>
<td>2.068(5)</td>
<td>2.067</td>
<td>2.061</td>
<td>2.045</td>
</tr>
<tr>
<td>6 Ir–N1</td>
<td>2.143(6)</td>
<td>2.234</td>
<td>2.319</td>
<td>2.242</td>
</tr>
<tr>
<td>Ir–N2</td>
<td>2.055(7)</td>
<td>2.080</td>
<td>2.088</td>
<td>2.078</td>
</tr>
<tr>
<td>Ir–N3</td>
<td>2.074(7)</td>
<td>2.103</td>
<td>2.137</td>
<td>2.102</td>
</tr>
<tr>
<td>Ir–C1</td>
<td>2.064(5)</td>
<td>2.091</td>
<td>2.074</td>
<td>2.044</td>
</tr>
<tr>
<td>Ir–C2</td>
<td>2.007(3)</td>
<td>2.025</td>
<td>1.979</td>
<td>2.044</td>
</tr>
<tr>
<td>Ir–C3</td>
<td>2.069(7)</td>
<td>2.067</td>
<td>2.027</td>
<td>2.045</td>
</tr>
</tbody>
</table>

* The Ir–N1 distance is not given for the 3MC_Carbene state because the pyridine ring of the ancillary ligand is decoordinated in this state.

Fig. 5 Schematic diagram showing the electronic density contours (0.05 e/bohr^3) and the energy values (in eV) calculated for the frontier molecular orbitals of complexes 5 and 6. H and L denote HOMO and LUMO, respectively.

Fig. 5 displays the energy and the atomic orbital composition of the highest-occupied and lowest-unoccupied molecular orbitals (HOMOs and LUMOs) for complexes 5 and 6. As expected, the HOMO of all complexes is composed of a mixture of Ir d orbitals and phenyl p orbitals distributed among the two ppy ligands. Upon the attachment of electron-withdrawing groups such as fluorine (3 and 4) and ester groups (3 and 6) to the cyclometallated ligands, the HOMO level becomes stabilized following the sequence: 5 (−5.63 eV), 6 (−5.73 eV), 4 (−5.98 eV) and 3 (−6.18 eV), which is in good agreement with the more positive oxidation potentials measured experimentally (5: +0.86 V, 6: +0.94 V, 4: +1.19 V, 3: +1.38 V). The HOMO stabilization computed on going from 5 to 3 (0.55 eV) is very close to the increase of the oxidation potential (0.52 V) and is due both to the presence of the fluorine substituents, which stabilizes the HOMO by 0.35 eV as obtained for 4, and to the attachment of the ester groups. In complex 6 ester groups are attached to the pyridine rings of the main ligand and only remotely influence the orthometallated phenyls where the electron density is located in the HOMO.

Theoretical calculations show that the LUMO of 5 resides on the ancillary ligand showing no overlap with the HOMO (Fig. 5). In contrast, the LUMO+1 and LUMO+2, which are slightly above the LUMO (0.03 and 0.15 eV, respectively), are mainly located on the pyridine rings of the cyclometallated ligands. Similar results are obtained for complex 4, for which the LUMO is slightly stabilized (−1.84 eV) compared with 5 (−1.72 eV). This stabilization supports the less negative reduction potential measured in passing from 5 (−2.43 V) to 4 (−2.26 V). In contrast to complexes 4 and 5, the LUMO of complex 6 is located on the main ligand due to the strong stabilization that the attachment of ester groups to the pyridine rings of the main ligands causes on the LUMO+1 and LUMO+2 of 5 (see Fig. 5). The LUMO+2 of complex 6 (−1.78 eV) resides on the ancillary ligand and lies at similar energies to the LUMO level of complex 5 (−1.72 eV) because the ester groups slightly affect the ancillary ligand. The lowering of the LUMO energy (0.65 eV) predicted in passing from 5 to 6 is in perfect agreement with the anodic shift of the first reduction potential (0.62 V) measured experimentally. The LUMO of complex 3 (−1.95 eV) is also located on the main ligand and appears at intermediate energies between the LUMO of 5 (−1.72 eV) and 6 (−2.37 eV) in accordance with the reduction potentials recorded experimentally (Table 3).

The energies calculated for the HOMO and the LUMO indicate a significant reduction of the HOMO–LUMO energy gap along the series 3 (4.24 eV), 4 (4.14 eV), 5 (3.91 eV) and 6 (3.36 eV), in good agreement with the red shift observed along this series in both absorption and emission spectra. However, the atomic orbital composition calculated for the LUMO does not support the fact that emission takes place from the main ligand, as experiment suggests, since, depending on the complex, the LUMO is located on the ancillary ligand (4 and 5) or on the main ligands (3 and 6). As the simple description of the HOMO and LUMO is not always representative of the emitting triplet state, the low-lying triplet states of complexes 3, 4, 5 and 6 were calculated using the time-dependent DFT (TD-DFT) as a first approach to further investigate the nature of the emitting excited state. Table 6 summarizes the characteristics of the lowest triplet states computed for these complexes at the optimized geometry of the ground state (S0).

TD-DFT calculations predict that the lowest-energy triplet state (T1) shows a similar nature for the four complexes (Table 6). It is described as a mixture of metal-to-ligand charge transfer (MLCT) and ligand-centered (LC) character since the monocyclic excitations that define T1 involve the HOMO and HOMO−1, which are mixtures of Ir d orbitals and ppy π orbitals, and the LUMO of the cyclometallated ligand, that corresponds to the LUMO in 3 and 6 and to the LUMO+1 in 4 and 5. The first excited triplet implying the N=C: ancillary ligand (T1 for 3, 4 and 5 and T5 for 6) is well separated (0.3–0.7 eV) from T1. TD-DFT calculations therefore suggest that the lowest-energy triplet of this series of compounds mainly involves the cyclometallated ligand.
calculated for the optimized T1 state indicates that excitation to T1
the most stable triplet for the four complexes. The spin density
implies an electron promotion from the Ir-ppy environment to the
and the Ir metal core, in contrast to what is found for complexes
bearing N’N ancillary ligands.10,22,36
To further investigate the nature of the lowest-energy triplet
state, the geometry of this state was optimized using the spin-
unrestricted DFT approach. After full-geometry relaxation, the
state, the geometry of this state was optimized using the spin-
unrestricted DFT approach. After full-geometry relaxation, the
state, the geometry of this state was optimized using the spin-
unrestricted DFT approach. After full-geometry relaxation, the
state, the geometry of this state was optimized using the spin-
unrestricted DFT approach. After full-geometry relaxation, the
state, the geometry of this state was optimized using the spin-

| Table 6 | Lowest triplet excited states calculated at the B3LYP(6-31G*+LANL2DZ) level for complexes 3, 4, 5 and 6. Vertical excitation energies (E),
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E (eV)</td>
<td>Monoexcitations</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>3</td>
<td>T1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>T1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>T1</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* MLCT, LC and LLCT denote metal-to-ligand charge transfer, ligand-centered and ligand-to-ligand charge transfer, respectively.

and the Ir metal core, in contrast to what is found for complexes
bearing N’N ancillary ligands.10,22,36
To further investigate the nature of the lowest-energy triplet
state, the geometry of this state was optimized using the spin-
unrestricted DFT approach. After full-geometry relaxation, the
T1 state defined by the TD-DFT calculations continues to be
the most stable triplet for the four complexes. The spin density
calculated for the optimized T1 state indicates that excitation to T1
implies an electron promotion from the Ir-ppy environment to the
cyclometallated ligands. This is illustrated in Fig. 6 for complexes
4, 5 and 6, for which the unpaired-electron spin density distribution
perfectly matches the topology of the monoelectronic excitations
in which the T1 state originates (HOMO → LUMO for 3 and 6,
and HOMO → LUMO+1 for 4 and 5). The electron promotion
associated with the excitation to T1 causes small changes (0.01–
0.02 Å) in the coordination sphere of the complex (Table 5). T1 is
computed to lie 2.84 (3), 2.84 (4), 2.69 (5) and 2.51 eV (6) above
S0 (adiabatic energy differences, ΔE in Fig. 6).
The nature of the T1 state can therefore be described as a mixed
3MLCT/3LC state with no participation of the N’C: ancillary
ligand (see Fig. 6). The calculated spin densities show an increase
of the metal contribution (MLCT character) on going from 3
to 6 (Ir: 0.10, ligand: 1.90 for 3; Ir: 0.37, ligand: 1.63 for 4;
Ir: 0.38, ligand: 1.62 for 5; and Ir: 0.45, ligand: 1.55 for 6) as
anticipated from the photophysical results. The large LC character
of the emitting state explains the structured aspect of the emission
band observed for complexes 3, 4 and 5 (Fig. 4). To estimate the
phosphorescence emission energy, the vertical energy difference
between T1 and S0 was computed by performing a single-point
calculation of S0 at the optimized minimum-energy geometry of T1
(Fig. 6). Calculations lead to vertical emission energies of 2.46 eV
for 3, 2.48 eV for 4, 2.39 eV for 5 and 2.20 eV for 6, in reasonably
good agreement with the experimental values for the maximum
emission (Table 3).

One of the most important deactivation pathways of the phosphorescent emission from T1 in transition-metal complexes
is the population of the metal-centered (3MC) triplet excited states.41,46-49 Metal-centered states result from the excitation of an
electron from the occupied t2g (dτ) HOMO to the unoccupied eg (dσ*) orbitals of the metal. As sketched in Fig. 7, dσ* orbitals involve σ-antibonding interactions between the iridium core and
the nitrogen atoms of either the ancillary or the cyclometallated
ligands. Two different types of 3MC states, here named 3MCcarbon and 3MCpy, result from these interactions which involve the
decoordination of one (3MCcarbene) and two (3MCpy) Ir–N bonds
leading to five- and four-coordinated structures in the excited state, respectively.
The geometries of both 3MC states (3MCcarbon and 3MCpy) were fully relaxed starting from the optimised geometry of S0 and
lengthening the respective Ir–N bond distances to 2.70 Å. Similar
optimized structures were obtained for the four complexes (see

Fig. 6 | Schematic energy diagram showing the adiabatic energy difference (ΔE) between S0 and T1 and the emission energy (Eem) from T1 calculated
for complexes 4, 5 and 6. The unpaired-electron spin-density contours (0.005 e.bohr−3) computed for the optimized T1 state are also shown.
Fig. 7  Top: Electron density contours (0.04 e bohr\(^{-3}\)) calculated for the unoccupied \(\epsilon_g\) molecular orbitals of 5 showing \(\sigma\)-antibonding interactions along the vertical \(N_{ppy}\)–Ir–\(N_{ppy}\) axis (left) and with the \(N\)–C: ancillary ligand (right). Bottom: Minimum-energy structures calculated for the \(^3MC_{ppy}\) (left) and \(^3MC_{carbene}\) (right) states of 5.

Table 5). As expected, the most important structural change found for the \(^3MC_{ppy}\) state concerns the Ir–\(N_{ppy}\) bonds, whose values lengthen by 0.3–0.7 Å compared to \(S_0\) and range between 2.35 and 2.75 Å. For the \(^3MC_{carbene}\) state, the pyridine ring of the ancillary ligand twists around the inter-ring bond by 60–75° and the nitrogen atom is fully decoordinated (see Fig. 7 bottom). The molecular structures calculated for both \(^3MC\) states are in good agreement with those obtained for similar iridium(III) complexes. The rupture of the metal–ligand bonds and, consequently, the opening of the coordination sphere enhances the reactivity of the complex and facilitates its degradation. The spin densities calculated for the \(^3MC_{ppy}\) and \(^3MC_{carbene}\) states (Fig. 8) reflect the \(\sigma\)-interactions that characterize these states and corroborate their metal-centered character.

More relevant than the molecular structure is the relative energy position of the \(^3MC\) states with respect to \(T_1\). After geometry relaxation, the \(^3MC_{carbene}\) state is calculated to lie below the \(T_1\) state (0.2–0.3 eV for 3, 4 and 5 and only 5 \(\times\) 10\(^{-4}\) eV for 6), while the \(^3MC_{ppy}\) state is located above the emitting state (~0.10 eV for 3, 4 and 5 and 0.87 eV for 6). Therefore, calculations suggest that both \(^3MC\) states could be thermally populated and play a role in the deactivation of the emission process. This would explain the poor photophysical properties obtained in this series of compounds. However, the theoretical data only concerns the relative adiabatic position of the \(^3MC\) states with respect to \(T_1\) and additional experimental studies, such as temperature-dependent analysis of the emitting excited-state lifetime, are needed to evaluate the activation energy barriers for populating the \(^3MC\) states. Progress in this direction is underway.

Electroluminescent properties

Finally we performed initial tests of complexes 4 (blue), 5 (green) and 6 (red) in simple devices as required colors for white. LEC devices incorporating the carbene-based complex materials were fabricated via spin-coating under ambient conditions on patterned indium tin oxide (ITO)-covered glass substrates. Prior to the deposition of the emitting layer a 100 nm layer of poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) PEDOT:PSS was deposited to planarize the ITO anode, increasing the yield and reproducibility of working devices. The emitting layer was prepared by dissolving six percent by weight of the corresponding complex and the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF\(_6\)] in a molar ratio of 3:1 in 0.5 mL of acetonitrile. [BMIM][PF\(_6\)] was used to enhance the ionic conductivity of the active layer accompanied with a reduction of the turn-on time of the device. The solutions were filtered using a 0.1 µm PTFE-filter and spin-coated on top of the PEDOT: PSS layer. Afterwards, the substrate was transferred to a nitrogen filled glovebox (O\(_2\) and H\(_2\)O < 1 ppm) and annealed on a hotplate at 100 °C for 1 h resulting in an emitting layer thickness of 150 nm. Finally, a 150 nm thick aluminum (Al) cathode was thermally evaporated on top under high vacuum (<10\(^{-6}\) mbar) using a shadow mask, defining 8 pixels per substrate, each having an active lighting area of 4 mm\(^2\). The device was encapsulated by a glass capping layer to protect the organic layers against penetrating oxygen and water.

Fig. 9 displays the electroluminescent spectra measured for complexes 4, 5 and 6 at a fixed voltage of 8 V. The spectra were recorded immediately after emission could be observed. The
devices with 4 and 5 exhibit green electroluminescence with a maximum located at around 512 and 544 nm, respectively, whereas for the device with 6 an orange emission is observed with an electroluminescence maximum at around 584 nm.

Upon applying a bias to the LEC devices, light emission slowly increases in intensity with time. The emission is characterized by a slow increase of both current density and luminance, due to the slow movement of the counter-ions to the interfaces of the electrodes which assists in the charge injection process as described for LECs based on ruthenium and iridium complexes. In our devices, the luminance values are very different for the three complexes. Devices with 4 and 5 present a low luminance and efficiency values at around 20 cd m$^{-2}$ and 10$^{-3}$ cd A$^{-1}$ at 6 V, while the device with 6 is very bright (1070 cd m$^{-2}$) and efficient 4.7 cd A$^{-1}$ at the same voltage. Additionally, the electroluminescence spectra observed for complexes 4 and 5 are strongly red-shifted with respect to the PL spectra obtained in solution (Fig. 4 and 9). This behavior has already been observed in other LEC devices and should be ascribed to either a polarization effect due to electrical excitation or a change of emissive excited state in solid-state. Ongoing accurately photophysical and device studies are being carried out to unveil the underlying reason of both the low performance level and the red-shift EL emission observed in LECs with 4 and 5.

Conclusions

In conclusion, we have developed a new family of electroactive charged bis-cyclometallated iridium(III) complexes based on pyridine-carbene as neutral ancillary ligand that emit from near-UV to red. This design holds great promise for developing deep-blue- and deep-red-emitting charged iridium complexes suitable for LECs applications. This is due to the emitting excited state being localized on the main C–N ligands, which therefore control the emitting properties of the complex. This represents a paradigmatic shift from usual charged complexes based on N–N ancillary ligands forming a five-membered ring with the central metal cation, where the emission properties are largely controlled by the ancillary ligand.

Experimental procedures

Materials and methods

Iridium trichloride hydrate was purchased from Heraeus. All solvents were used as pa grade and degassed by three consecutive vacuum and back-fill cycles. 3-Methyl-1-(4-methyl-2-pyridyl)benzimidazolium iodide (pmbi), 2,6-difluoro-2,3-bipyridine and [Ir(C=C,N)(μ-Cl)]$^+$ were prepared according to literature procedures. All other materials and solvents were of reagent quality and used as received. H and 13C NMR spectra were recorded using a Bruker AV 400 MHz spectrometer. Chemical shifts δ (in ppm) are referenced to residual solvent peaks. For 1H NMR: CDCl$_3$, 7.24 ppm; for 13C NMR: CDCl$_3$, 77.0 ppm. 19F and 31P NMR were recorded using a Bruker AV 200 MHz spectrometer. Coupling constants are expressed in hertz (Hz). High-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF-MS instrument using electrospray ionisation (ESI). UV-visible spectra were recorded in a 1 cm path length quartz cell on a Cary 100 spectrophotometer. Emission spectra were recorded on a Fluorolog 3–22 using a 90° optical geometry. The photoluminescence quantum yields were determined using quinine sulfate (10$^{-3}$ M in 1 N H$_2$SO$_4$; air equilibrated; $Φ_1$ = 0.546) and [Ru(bpy)$_3$]$_2^+$ (10$^{-5}$ M in water; air equilibrated; $Φ_1$ = 0.028) as standards. Excited-state lifetimes were measured using a FL-1061PC TCSPC and 371 and 406 nm Nanoleo as excitation source. Voltammetric measurements employed a PC controlled AutoLab PSTAT10 electrochemical workstation and were carried out in an Ar-filled glove box, oxygen and water < 1 ppm. Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) techniques were used to estimate the redox potentials. DPV was used in support for CV to obtain a better estimate of the electrochemical potentials when the systems show behavior near to the irreversibility, i.e. one of the two peaks in the CV is not well defined. DPVs were carried out sweeping from negative to positive potentials and mean values are calculated. CVs were obtained at a scan rate of 1 and 0.1 V s$^{-1}$. DPVs were obtained at a Modulation Potential of 50 mV, a Step Potential of 10 mV, a Modulation Time of 50 ms and an Interval Time of 100 ms. Measurements were carried out using 0.1 M TBAPF$_6$ as supporting electrolyte in acetonitrile (MeCN). Glassy carbon, platinum plate and platinum wire were used as working, counter and quasi-reference electrodes, respectively. At the end of each measurement, ferrocene was added as an internal reference. Data collections for X-ray crystal structures were performed at low temperature [100(2) K] using Mo-Kα radiation on a Bruker APEX II CCD, having kappa geometry. All data sets were reduced by means of EvalCCD$^{44}$ and then corrected for absorption.$^{35}$ The solutions and refinements were performed by SHELX.$^{36}$ The crystal structures were refined using full-matrix least-squares based on F$^2$ with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the “riding” model.

Computational details

Density Functional Theory (DFT) calculations were carried out with the D02 revision of the Gaussian 03 program package,$^{37}$ using Becke’s three-parameter B3LYP exchange-correlation functional$^{38,39}$ together with the 6-31G** basis set for C, H, O, F and N atoms$^{40}$ and the “double-ξ” quality LANL2DZ basis set for the Ir element.$^{41}$ An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core ([5s]$^2$([5p]$^3$) electrons and the (5d)$^6$ valence electrons of Ir(n)). The geometries of the singlet ground state (S$_0$) and of the lowest triplet excited state (T$_1$) were fully optimized. Triplet states were calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. The expected values calculated for S$^*$ were always smaller than 2.05. Solvent effects were considered within the SCRF (self-consistent reaction field) theory using the polarized continuum model (PCM) approach to model the interaction with the solvent.$^{42,43}$ Molecular orbitals were calculated in acetonitrile using gas-phase optimized geometries. Starting from the closed-shell S$_0$ state, time-dependent DFT (TD-DFT) calculations$^{44,46}$ were performed in acetonitrile solution to determine the energies and the electronic nature of the lowest excited triplet states at the ground-state geometry. Vertical electronic excitation energies were determined for the lowest 10 triplet states.
General procedure for the preparation of Ir carbene complexes

A solution of 74 mg (0.21 mmol, 2.1 eq) of 3-methyl-1-(4-methyl-2-pyridyl)benzimidazolium iodide, 28 mg (0.12 mmol, 1.2 eq) of silver(I) oxide, and 0.10 mmol (0.5 eq) of the corresponding iridium dimer in 12 mL of 1,2-dichloroethane was degassed (3 vacuum and back-fill cycles) and heated to reflux (95 °C) overnight. After cooling to ambient temperature, the mixture was filtered through celite to remove silver residues. The celite was washed with CHCl₃ and the solvent was removed in vacuo. The residue was redissolved in 20 mL of CHCl₃ and extracted three times with an aqueous KPF₆ solution (55 mg of KPF₆ in 40 mL of water per cycle). The combined organic layers were washed with water, dried over MgSO₄ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel using CHCl₃ and then CHCl₃/acetone (p.a. grade) 4/1 as solvent. After evaporation of the solvent the pure product was obtained.

[(1-2,4-difluoropheny]-1H-pyrazole),Ir(pmbi)]PF₆ 4

Yellow solid. Yield: 93 mg (0.10 mmol, 50%). ¹H NMR (400 MHz, CDCl₃); δ 8.30 (dd, J_{HH} = 8.0 Hz, 3H, ArH), 8.27 (s, 1H, ArH), 7.95 (bd, J_{HH} = 5.8 Hz, 1H, ArH), 7.81–7.76 (m, 2H, ArH), 7.61–7.57 (m, 3H, ArH), 7.47–7.42 (m, 2H, ArH), 7.12–7.02 (m, 3H, ArH), 6.60–6.48 (m, 2H, ArH), 5.79 (dd J_{HH} = 8.6 Hz, J_{HF} = 2.3 Hz, 1H, ArH), 5.58 (dd, J_{HH} = 7.7 Hz, J_{HF} = 2.3 Hz, 1H, ArH), 3.43 (s, 3H, CH₃), 2.68 (s, 3H, CH₃). ¹⁹F NMR (81 MHz, CDCl₃); δ −144.6 (sept, J_{PF} = 713 Hz, PF₆). ¹³C NMR (188 MHz, CDCl₃); δ −73.3 (d, J_{PF} = 712 Hz, PF₆), −105.3 (q, J = 9.1 Hz, ArF), −105.7 (q, J = 9.5 Hz, ArF), −108.0 (vt, J = 11.7 Hz, ArF). HRMS (ESI-TOF) m/z (%); calcld. 928.1677; found 928.1670 (100) [(M−PF₆)⁺].

[(2-phénylpyridine),Ir(pmbi)]PF₆ 5

Yellow solid. Yield: 165 mg (0.19 mmol, 95%). ¹H NMR (400 MHz, CDCl₃); δ 8.29 (d, J_{HH} = 8.4 Hz, 1H, ArH), 8.23 (s, 1H, ArH), 7.95 (bd, J_{HH} = 5.1 Hz, 1H, ArH), 7.90 (bt, J_{HH} = 6.8 Hz, 2H, ArH), 7.76–7.71 (m, 2H, ArH), 7.68 (bt, J_{HH} = 6.9 Hz, 2H, ArH), 7.60 (bd, J_{HH} = 5.7 Hz, 1H, ArH), 7.57 (bt, J_{HH} = 6.8 Hz, 2H, ArH), 7.45–7.39 (m, 2H, ArH), 7.06–6.94 (m, 6H, ArH), 6.86 (dt, J_{HH} = 5.0 Hz, J_{HF} = 1.3 Hz, 1H, ArH), 6.40 (dd, J_{HH} = 7.6 Hz, J_{HF} = 0.9 Hz, 1H, ArH), 6.18 (dd, J_{HH} = 7.3 Hz, J_{HF} = 1.0 Hz, 1H, ArH), 3.35 (s, 3H, NCH₃), 2.66 (s, 3H, CH₃). ¹⁹F NMR (81 MHz, CDCl₃); δ −144.5 (sept, J_{PF} = 713 Hz, PF₆). ¹³C NMR (188 MHz, CDCl₃); δ −73.4 (d, J_{PF} = 712 Hz, PF₆). HRMS (ESI-TOF) m/z (%); calcld. 724.2052; found 724.2054 (100) [(M−PF₆)⁺].

[(Methyl 2-phenylisonicotinate),Ir(pmbi)]PF₆ 6

Orange solid. Yield: 167 mg (0.17 mmol, 85%). ¹H NMR (400 MHz, CDCl₃); δ 8.44 (d, J_{HH} = 14.7 Hz, 2H, ArH), 8.25 (d, J_{HH} = 8.3 Hz, 1H, ArH), 8.22 (s, 1H, ArH), 8.15 (d, J_{HH} = 6.0 Hz, 1H, ArH), 7.79 (bt, J_{HH} = 6.8 Hz, 3H, ArH), 7.52–7.49 (m, 4H, ArH), 7.41 (bt, J_{HH} = 8.3 Hz, 2H, ArH), 7.08 (bt, J_{HH} = 7.6 Hz, 1H, ArH), 6.98 (m, 3H, ArH), 6.89 (bt, J_{HH} = 7.3 Hz, 1H, ArH), 6.38 (d, J_{HH} = 7.6 Hz, 1H, ArH), 6.15 (d, J_{HH} = 7.4 Hz, 1H, ArH), 3.94 (s, 6H, OCH₃), 3.33 (s, 3H, CH₃), 2.63 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃); δ 187.1 (NCN), 169.7 (COOME), 168.3 (COOME), 164.5, 164.4, 163.9, 153.4, 154.1, 154.0, 149.6, 149.5, 149.4, 143.2, 141.8, 138.9, 138.3, 136.3, 131.7, 131.4, 131.2, 131.1, 130.8, 126.1, 125.5, 125.5, 125.0, 123.6, 123.5, 122.4, 122.2, 119.6, 119.2, 114.4, 113.1, 111.8 (ArC), 53.2 (OMe), 53.1 (OMe), 33.7 (NMe), 29.9 (Me). ¹⁹F NMR (81 MHz, CDCl₃); δ −144.6 (sept, J_{PF} = 713 Hz, PF₆). ¹³F NMR (188 MHz, CDCl₃); δ −73.3 (d, J_{PF} = 712 Hz, PF₆). HRMS (ESI-TOF) m/z (%); calcld. 840.2162; found 840.2164 (100) [(M−PF₆)⁺].

[(Methyl 2-phenanthren-9-yl)isonicotinate],Ir(pmbi)]PF₆ 7

Red solid. Yield: 130 mg (0.11 mmol, 55%). ¹H NMR (400 MHz, CDCl₃); δ 8.85 (s, 1H, ArH), 8.79 (s, 1H, ArH), 8.52–8.36 (m, 6H, ArH), 8.15–8.11 (m, 2H, ArH), 8.05 (d, J_{HH} = 6.1 Hz, 1H, ArH), 7.75–7.70 (m, 2H, ArH), 7.64–7.58 (m, 2H, ArH), 7.52–7.48 (m, 4H, ArH), 7.43–7.30 (m, 6H, ArH), 6.91–6.76 (m, 3H, ArH), 6.85 (dd, 1H, ArH), 7.95 (dd, 1H, ArH), 7.34–7.26 (m, 3H, ArH), 7.25–7.15 (m, 3H, ArH), 7.15–7.10 (s, 1H, ArH). HRMS (ESI-TOF) m/z (%); calcld. 912.1785; found 912.1788 (100) [(M−PF₆)⁺].
Device preparation and characterization

Poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) aqueous dispersion (PEDOT:PSS) (CleviosTM P VP AI4083) was purchased from Heraeus (formerly H. C. Starck). Acetonitrile (anhydrous, 99.8%) and 1-butyl-3-methyl-imidazolium hexafluorophosphate [BMIM][PF6] (purrum, ≥97.0%) were obtained from Sigma Aldrich and were used as received. Indium tin oxide (ITO)-coated glass plates were patterned using conventional photolithography. Before deposition of the organic layers, the substrates were extensively cleaned using sonification in detergent baths and subsequent oxygen plasma treatment. The thicknesses of the films were determined using a KLA Tencor P-15 profilometer. The electro-optical characterization was carried out in a Botest Char, 14944. This journal is © the Royal Society of Chemistry 2012