Preparation of Phosphorescent Iridium(III)

Complexes with a Dianionic C,C,C,C-Tetradentate Ligand

Miguel A. Esteruelas,*a Ana M. López,a Enrique Oñate,a Ainhoa San-Torcuato,a Jui-Yi Tsai,b and Chuanjun Xiaa

aDepartamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Zaragoza - CSIC, 50009 Zaragoza (Spain)

bUniversal Display Corporation, 375 Phillips Boulevard, Ewing, New Jersey 08618 (USA).

ABSTRACT The preparation and photophysical properties of heteroleptic iridium(III) complexes, containing a dianionic C,C,C,C-tetradentate ligand and a cyclometalated phenylpyridine group are described. Complex [Ir(µ-OMe)(COD)]2 (1, COD = 1,5-cyclooctadiene) reacts with 1,1-diphenyl-3,3-butylenedimidazolium iodide
([PhIm(CH$_2$)$_4$ImPh]I$_2$), in the presence NaO'tBu, to give [Ir($\mu$-I){κ$^4$-C,C,C,C-[C$_6$H$_4$Im(CH$_2$)$_4$ImC$_6$H$_4$]}]: (2), which leads to {{Ir{κ$^4$-C,C,C,C-[C$_6$H$_4$Im(CH$_2$)$_4$ImC$_6$H$_4$]}]$\mu$-OH}{$\mu$-OMe}} (3) by treatment firstly with silver trifluoromethanesulphonate (AgOTf) in acetone-dichloromethane and subsequently with KOH in methanol. The reaction of 2 with AgOTf and acetonitrile affords the bis(solvento) complex [Ir{κ$^4$-C,C,C,C-[C$_6$H$_4$Im(CH$_2$)$_4$ImC$_6$H$_4$]}(CH$_3$CN)$_2$]OTf (4). The latter promotes the pyridyl-supported heterolytic ortho-CH bond activation of the phenyl group of 2-phenylpyridine, 2-(2,4-difluorophenyl)pyridine, 2-(p-tolyl)pyridine and 5-methyl-2-phenylpyridine to yield Ir{κ$^4$-C,C,C,C-[C$_6$H$_4$Im(CH$_2$)$_4$ImC$_6$H$_4$]}{κ$^2$-C,N-[Ar-py]} (Ar-py = C$_6$H$_4$-py (5), C$_6$H$_4$F$_2$-py (6), C$_6$H$_4$Me-py (7), C$_6$H$_4$-Mepy (8)) using (piperidinomethyl)polystyrene as an external base. Complexes 5–8 are blue-green emitters, which display short lifetimes (0.6–4.8 μs) and quantum yields close to the unity in both doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in 2-methyltetrahydrofuran at room temperature.

INTRODUCTION

The straightforward manner in which the photophysical properties of phosphorescent emitters can be tuned by combining different ligands in the coordination sphere of the metal center has positioned the heteroleptic iridium(III) complexes at the forefront of modern photochemistry. As a consequence, several classes of compounds of this type have been reported, being the focus mainly centered on [3b+3b+3b$^+$] derivatives which are easily obtained via [Ir($\mu$-Cl)(3b)$_2$]: dimers. Because each compound has its own photophysical properties, the development of heteroleptic emitters undergoes two main problems: the existence of several isomers with
different stereochemistry for a given stoichiometry and their marked trend to reach the ligands redistribution equilibrium.⁴

A promising strategy to mitigate these problems is to link the donor groups coordinated at the metal center. The generation of ligands with higher denticity reduces both the number of possible isomers and the number of compounds in the mixtures due to ligand redistribution issues. Furthermore, recent studies indicate that the link favors narrow and bluer emissions. This, which is highly desirable for OLED display applications, seems to be related to less pronounced differences between the excited-state structure and the ground-state structure.¹⁵

Cyclometalated phenylpyridines were initially the most used 3b ligands.⁶ However, they are being replaced by cyclometalated aryl-N-heterocyclic carbenes (Ar-NHCs) because of the latter effectively raise the LUMO energy, which gives rise to a wider band gap and therefore more energetic emissions. In addition, their electronic properties ensures that deactivating ligand-field states remain higher in energy than the emissive triplet state.⁷ The applicability of NHC groups needs their coordination, which requires specific procedures. In this context, the cleanest method is the direct metalation of imidazolium or benzimidazolium salts.⁸ If one links two cyclometalated Ph-NHC groups with a flexible chain, through the nitrogen atoms, one can generate a dianionic C,C,C,C-tetradentate ligand and therefore [6tt+3b] (tt = tetradentate) phosphorescent heteroleptic iridium(III) derivatives.

Tetradentate ligands are less common than those with one, two, or three donor atoms and carbon is also a less frequent donor atom than nitrogen, phosphorus, arsenic, oxygen, or sulfur.⁹ Thus, although the boom of the NHCs has given rise in recent years to interesting complexes containing tetradentate ligands based on one, two, three, and four NHC groups, those coordinating four C-donor atoms are very scarce.¹⁰ The great majority of C,C,C,C-donors ligands
are neutral macrocycles based on four NHC moieties, which coordinate to generate a plane (I),\textsuperscript{11} with some exceptions.\textsuperscript{12} A few acyclic system have been also described, which stabilize structures II\textsuperscript{13} (Chart 1).

**Chart 1. Structures Stabilized by C,C,C,C-Tetradentate Ligands**

![Chart 1](chart1.png)

The generation of tetradentate ligands based on two cyclometalated Ar-NHC moieties requires the chelating coordination of a bidentate bis(N-phenyl)-substituted-bis(NHC) ligand and the subsequent C-directed *ortho*-CH bond activation of both N-phenyl substituents.\textsuperscript{14} The chelating versus bridging coordination of bis(NHC) ligands is an unresolved issue.\textsuperscript{15} It has been suggested that the length of the linker between the azole rings plays a main role in the type of coordination.\textsuperscript{16} However, the problem is much more complex. Recently, we have shown that the d\textsuperscript{2}-hexahydride OsH\textsubscript{6}(PPr\textsubscript{3})\textsubscript{2} promotes the direct metalation of the benzimidazolium units and the *ortho*-CH bond activation of both phenyl substituents of 1,1'-diphenyl-3,3'-ethylenedibenzimidazolium to give Os\{κ\textsuperscript{4}-C,C,C,C-[C\textsubscript{6}H\textsubscript{4}BzIm(CH\textsubscript{2})\textsubscript{2}BzImC\textsubscript{6}H\textsubscript{4}]\}L\textsubscript{2} derivatives, containing a dianionic C,C,C,C-tetradentate ligand (Scheme 1).\textsuperscript{5b} In contrast to the d\textsuperscript{2}-hexahydride, the d\textsuperscript{1}-pentahydride IrH\textsubscript{5}(PPr\textsubscript{3})\textsubscript{2} reacts with 1,1'-diphenyl-3,3'-alkylenediimidazolium halides ([(CH\textsubscript{2})\textsubscript{n}(HImC\textsubscript{6}H\textsubscript{5})\textsubscript{2}]X\textsubscript{2}; \(n = 2, 3, 4\)) to yield the dinuclear derivatives \{[IrH\textsubscript{2}(PPr\textsubscript{3})\textsubscript{2}]\textsubscript{2}[μ-(CH\textsubscript{2})\textsubscript{n}(ImC\textsubscript{6}H\textsubscript{4})\textsubscript{2}]\} (\(n = 2, 3, 4\)), regardless of the length of the chain between the imidazolyldiene groups (Scheme 2),\textsuperscript{17} although the steric hindrance of both polyhydrides is the same. The tetradentate ligand of Os\{κ\textsuperscript{4}-C,C,C,C-[C\textsubscript{6}H\textsubscript{4}BzIm(CH\textsubscript{2})\textsubscript{2}BzImC\textsubscript{6}H\textsubscript{4}]\}L\textsubscript{2} avoids a four-planar coordination, whereas it favors sawhorse-type dispositions (II and III in Chart 1). The reason for this preference appears to be electronic,
because the observed arrangement for the donor atoms is not determined by the presence of the linker between the benzimidazolylidene groups and is as that found in complexes containing two independent orthometalated N-phenylbenzimidazolylidene ligands.\textsuperscript{5b}

**Scheme 1. Reaction of OsH\textsubscript{6}(P\textsuperscript{3}Pr\textsubscript{3})\textsubscript{2} with 1,1’-Diphenyl-3,3’-ethylenedibenzimidazolium\textsuperscript{5b}**

![Scheme 1](image)

**Scheme 2. Reactions of IrH\textsubscript{5}(P\textsuperscript{3}Pr\textsubscript{3})\textsubscript{2} with 1,1’-Diphenyl-3,3’-alkylenediimidazolium\textsuperscript{17}**

![Scheme 2](image)

This paper shows an entry to iridium(III) emitters of the class [6tt+3b], which display quantum yields close to the unity, and at the same time demonstrates that the synthetic precursor plays a key role in the coordination mode of tetradeinate bis(N-phenyl)-bis(NHC) ligands.

**RESULTS AND DISCUSSION**

**The Synthetic Precursor.** Dimers [Ir(μ-Cl)(κ\textsuperscript{2}-C,C-(C\textsubscript{6}R\textsubscript{4}-NHC))\textsubscript{2}]: have shown to be useful synthetic precursors to prepare iridium(III) emitters of the class [3b+3b+3b’], with two cyclometalated Ar-NHC ligands, which are the counterparts of our target [6tt+3b] compounds. They are usually obtained from the reactions of the known complex [Ir(μ-Cl)(COD)]; (COD = 1,5-cyclooctadiene) with the corresponding imidazolium or benziimidazolium chloride in the
presence of a base and their X-ray structures reveal that the NHC groups are mutually trans disposed at the coordination sphere of each iridium(III).\textsuperscript{7b,c} As a consequence, the resulting [3b+3b+3b’] derivatives also show a mutually trans NHC arrangement.\textsuperscript{7d-f,i} We decided to explore this synthetic strategy to prepare [6tt+3b] derivatives containing two cyclometalated Ar-NHC moieties linked by a butylene chain, given that the use of the pentahydride IrH\textsubscript{5}(PPr\textsubscript{3})\textsubscript{2} as synthetic precursor had previously led to a compound with a bridging bis(NHC) ligand.\textsuperscript{17} However, a more suitable precursor than [Ir(μ-Cl)(COD)]\textsubscript{2} would be the methoxide-counterpart [Ir(μ-OMe)(COD)]\textsubscript{2} (1), since the methoxide ligand of this type of dimers has proven to allow the direct metalation of imidazolium and benzimidazolium salts.\textsuperscript{18}

Treatment of 2-methoxyethanol suspensions of 1 with 3.4 equivalents of 1,1’-diphenyl-3,3-butylenediimidazolium iodide ([PhIm(CH\textsubscript{2})\textsubscript{4}ImPh]I\textsubscript{2}), in the presence of sodium tert-butoxide (NaOtBu), at 130 °C, for 6 hours produces the precipitation of the dimer [Ir(μ-I){κ\textsuperscript{4}-C,C,C,C-[C\textsubscript{6}H\textsubscript{4}Im(CH\textsubscript{2})\textsubscript{4}ImC\textsubscript{6}H\textsubscript{4}]}\textsubscript{2} (2), as a white solid in 65% yield (Scheme 3). Interestingly, its \textsuperscript{13}C{\textsuperscript{1}H} NMR spectrum, in dichloromethane-\textit{d}\textsubscript{2}, at room temperature shows two resonances for the metalated NHC-carbon atoms, at 175.6 and 153 ppm, and two resonances for the metalated phenyl-carbon atoms, at 150.7 and 131.7 ppm. This reveals that the imidazolylidene units of 2 are mutually cis disposed, in contrast to that observed for related dimers containing two free cyclometalated Ar-NHC ligands. So, unlike the osmium complexes Os{κ\textsuperscript{4}-C,C,C,C-[C\textsubscript{6}H\textsubscript{4}BzIm(CH\textsubscript{2})\textsubscript{2}BzImC\textsubscript{6}H\textsubscript{4}]}L\textsubscript{2} shown in Scheme 1, the linker between the NHC units of 2 is determinant to place the donor atoms in their positions at the coordination sphere of the metal centers.
Scheme 3. Synthesis of the Precursors

Treatment of 2 firstly with silver trifluoromethanesulphonate (AgOTf) in acetone-dichloromethane and subsequently with KOH in methanol produces the replacement of the double iodide bridge by a mixed hydroxide-methoxide bridge. The resulting dimer \{[\text{Ir}^{κ^4-C,C,C,C-[C₆H₄Im(Im(CH₂)₄ImC₆H₄)]})\}_2(μ-OH)(μ-OMe)\} (3), was isolated in 47% yield, also as a white solid. Like for 2, the $^{13}$C{$^1$H} NMR spectrum of 3, in dichloromethane-$d_2$, at room temperature displays two resonances for the metalated NHC-carbon atoms, at 182.7 and 160.9 ppm, and two resonances for the metalated phenyl-carbon atoms, at 156.8 and 133.0 ppm, indicating that the arrangement of the C-donor atoms around the metal center of 2 is kept in 3. This was confirmed by means of the X-ray diffraction analysis of the structure of the latter (Figure 1). The structure has a $C_2$ axis, which contains the oxygen atoms of the bridge. As a consequence, the tetradentate ligands are oriented in anti-disposition. In agreement with the $^{13}$C{$^1$H} NMR spectra, the coordination polyhedron around each iridium atom can be described as a distorted octahedron with the imidazolylidene of a cyclometalated Ph-NHC moiety trans to the orthometalated phenyl of the other one (C7–Ir–C18 = 172.1(2)º), whereas the hydroxide
ligand lies *trans* to the remaining orthometalated phenyl (O1–Ir–C1 = 169.97(18)°) and the methoxide ligand is *trans* to the remaining imidazolylidene (O2–Ir–C14 = 168.81(18)°). The separation between the metal center and the phenyl *trans* to the hydroxide ligand (Ir–C1 = 2.019(5) Å) is about 0.05 Å shorter than the separation between the iridium atom and the phenyl *trans* to the imidazolylidene (Ir–C18 = 2.066(6) Å). Similarly, the separation between the metal center and the imidazolylidene *trans* to the methoxide ligand (Ir–C14 = 1.963(5) Å) is about 0.05 Å shorter than the separation between the iridium atom and imidazolylidene situated *trans* to the phenyl (Ir–C7 = 2.051(6) Å). The Ir–OH and Ir–OMe bond lengths of 2.190(4) (Ir–O1) and 2.123(3) (Ir–O2) Å, respectively, compare well with those reported for double hydroxide\textsuperscript{19} and methoxide\textsuperscript{20} bridges in iridium(III) complexes.

*Figure 1.* Molecular diagram of 3 (50% probability ellipsoids). Hydrogen atoms (except H1) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–C1 = 2.019(5), Ir–C7 = 2.051(6), Ir–C14 = 1.963(5), Ir–C18 = 2.066(6), Ir–O1 = 2.190(4), Ir–O2 = 2.123(3); C7–Ir–C18 = 172.1(2), O1–Ir–C1 = 169.97(18), O2–Ir–C14 = 168.81(18), C1–Ir–C18 = 93.3(2), C7–Ir–C14 = 97.6(2).
The removal of the iodide ligands of 2 with AgOTf in acetone-dichloromethane leads to a complex mixture of solvento species, which in acetonitrile affords the mononuclear bis(acetonitrile) derivative \([\text{Ir}\{\kappa^4-C,C,C,C-[\text{C}_6\text{H}_4\text{Im(CH}_2)_4\text{ImC}_6\text{H}_4]\}](\text{CH}_3\text{CN})_2]\)OTf (4). This salt was isolated as a white solid in 71% yield. The demolishing of the dinuclear structure does not give rise to any change in the disposition of the C-donor atoms of the tetradentate ligand. Thus, in agreement with 2 and 3, the \(^{13}\text{C}\{^1\text{H}\}\) NMR spectrum of 4, in dichloromethane-\(d_2\), at room temperature shows two resonances for the inequivalent metalated imidazolylidene carbon atoms, at 170.9 and 151.1 ppm, and two resonances for the inequivalent metalated phenyl carbon atoms, at 146.8 and 124.6 ppm.

**Preparation and Characterization of [6tt+3b] Complexes.** The bis(acetonitrile) complex 4 is an excellent synthetic precursor to prepare [6tt+3b] complexes containing a cyclometalated phenylpyridine ligand. The procedure implies pyridyl-supported heterolytic ortho-CH bond activation reactions, on the phenyl group, which use (piperidinomethyl)polystyrene as an external base. The reactions were carried out in fluorobenzene under reflux and are compatible with substituents at both the pyridyl and phenyl groups (Scheme 4). Thus, under the above mentioned conditions, the treatment of 4 with 1.0 equivalent of 2-phenylpyridine (\(\text{C}_6\text{H}_5\)-py), 2-(2,4-difluorophenyl)pyridine (\(\text{C}_6\text{H}_3\text{F}_2\)-py), 2-(p-toly)pyridine (\(\text{C}_6\text{H}_4\text{Me}\)-py), and 5-methyl-2-phenylpyridine (\(\text{C}_6\text{H}_5\)-Mepy) affords the respective derivatives \(\text{Ir}\{\kappa^4-C,C,C,C-[\text{C}_6\text{H}_4\text{Im(CH}_2)_4\text{ImC}_6\text{H}_4]\}\{\kappa^2-C,N-[\text{Ar-py}]\}\) (\(\text{Ar-py} = \text{C}_6\text{H}_5\)-py (5), \(\text{C}_6\text{H}_3\text{F}_2\)-py (6), \(\text{C}_6\text{H}_4\text{Me}\)-py (7), \(\text{C}_6\text{H}_5\)-Mepy (8)), which were isolated as analytically pure yellow solids in high yields (80–95%) without further purification.
Scheme 4. Preparation of [6tt+3b] Complexes

The stereochemistry of the obtained [6tt+3b] complexes was confirmed by means of the X-ray diffraction analysis of 5. Its structure (Figure 2) reveals that the relative disposition of the donor atoms of the tetradentate ligands does not change in the new octahedral environment, i.e., the imidazolylidene of a cyclometalated Ph-NHC unit is situated trans to the orthometalated phenyl of the other one (C25–Ir–C12 = 167.2(2)°). Furthermore, it proves that from the two possible isomers resulting from the cyclometalation of the phenylpyridine, pyridine trans to phenyl and pyridine trans to imidazolylidene, the latter is regioselectively formed with pyridine–iridium–imidazolylidene and phenyl–iridium–phenyl angles of 167.2(2) (N1–Ir–C18) and 170.9(2)° (C7–Ir–C29) respectively. The iridium–imidazolylidene distances of 1.956(6) (Ir–C18) and 2.072(6) (Ir–C25) Å and the iridium–phenyl bond lengths of 2.062(6) (Ir–C12), 2.090(6) (Ir–C7), and 2.115(6) (Ir–C29) Å compare well with those of 3.
Figure 2. Molecular diagram of 5 (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–N1 = 2.096(6), Ir–C7 = 2.090(6), Ir–C12 = 2.062(6), Ir–C18 = 1.956(6), Ir–C25 = 2.072(6), Ir–C29 = 2.115(6); N1–Ir–C18 = 167.2(2), C7–Ir–C29 = 170.9(2), C12–Ir–C25 = 167.2(2), N1–Ir–C7 = 78.9(2), C12–Ir–C18 = 79.7(2), C25–Ir–C29 = 77.8(2).

The $^{13}$C{¹H} NMR spectra 5–8, in dichloromethane-$d_2$, at room temperature are consistent with the structure shown in Figure 2 and agree well with those of 2–4. Thus, they show two resonances for the inequivalent metalated imidazolylidene carbon atoms, at about 176 and 165 ppm, and two resonances for the metalated carbon atoms of the inequivalent phenyl groups of the tetradentate ligand, between 152 and 155 ppm. The resonance corresponding to the metalated carbon atom of the bidentate C,N-donor ligand appears between 171 and 173 ppm for 5, 7, and 8 and at 179.8 ppm for 6.

As it has been previously mentioned, the [3b+3b+3b’] iridium complexes containing two free cyclometalated Ph-NHC ligands display octahedral environments with the NHC units disposed mutually trans. In this context, it should be pointed out that the linkage of the cyclometalated
moieties with a butylene chain allows to isolate species with an arrangement NHC trans to phenyl.

**Photophysical and Electrochemical Properties of the [6tt+3b] Complexes.** UV/vis absorption data of 1.0–6.5 × 10⁻⁵ M 2-methyltetrahydrofuran (MeTHF) solutions of complexes 5–8, at room temperature, are collected in Table 1. The spectra of the four complexes are similar (Figures S19 – S22 in the Supporting Information), showing three different zones: 230–300, 320–410, and >420 nm. Time-dependent DFT calculations (B3LYP-GD3//SDD(f)/6-31G**), computed in tetrahydrofuran as solvent, indicate that the absorptions at the highest energy region correspond mainly to ¹π–π* interligand and intraligand transitions. The bands in the region of moderate energy are due to allowed spin metal-to-phenylpyridine charge transfer (1MLCT) mixed with NHC-to-phenylpyridine transitions. The weak absorption tails after 420 nm are usually assigned to formally spin-forbidden 3MLCT transitions, caused by the large spin-orbit coupling introduced by the iridium center.²¹

The oxidation and reduction potentials of 5–8 were measured by cyclic voltammetry in degassed acetonitrile solutions and referenced vs Fc/Fc⁺. The data are collected on Table 2. The four complexes exhibit an irreversible oxidation peak potential in the region 0.23–0.41 V and a quasi-reversible reduction in the narrow region from −2.94 to −3.02 V. The electrochemical gap is in agreement with the calculated HOMO-LUMO gap (Table 2, Tables S10–S13, and Figures S23–S26) and with those previously reported for neutral iridium complexes containing two free cyclometalated NHC ligands with the NHC disposed mutually trans.⁷d,e,g
Table 1. Selected Experimental UV-Vis Absorptions for 5–8 (in MeTHF) and Computed TD-DFT (in THF) Vertical Excitation Energies and their Major Contributions

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{exp}$ (nm)</th>
<th>$\varepsilon \times 10^3$ (M$^{-1}$·cm$^{-1}$)</th>
<th>Excitation energy (nm)</th>
<th>Oscillator strength, $f$</th>
<th>Transition</th>
<th>Contrib (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>244</td>
<td>16.5</td>
<td>238</td>
<td>0.0678</td>
<td>HOMO-5 → LUMO+2</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>24.5</td>
<td>279</td>
<td>0.0684</td>
<td>HOMO-6 → LUMO</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>344</td>
<td>4.0</td>
<td>345</td>
<td>0.0495</td>
<td>HOMO-2 → LUMO</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>2.6</td>
<td>381</td>
<td>0.0250</td>
<td>HOMO-1 → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>402</td>
<td>2.1</td>
<td>409</td>
<td>0.0246</td>
<td>HOMO → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>444</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>234</td>
<td>94.1</td>
<td>242</td>
<td>0.0648</td>
<td>HOMO-4 → LUMO+3</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>56.8</td>
<td>278</td>
<td>0.1028</td>
<td>HOMO-6 → LUMO</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>324</td>
<td>12.3</td>
<td>336</td>
<td>0.0119</td>
<td>HOMO-3 → LUMO+1</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>342</td>
<td>6.7</td>
<td>343</td>
<td>0.0399</td>
<td>HOMO-2 → LUMO</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>374</td>
<td>3.8</td>
<td>374</td>
<td>0.0250</td>
<td>HOMO-1 → LUMO</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>2.7</td>
<td>401</td>
<td>0.0165</td>
<td>HOMO → LUMO</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>430</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>234</td>
<td>137</td>
<td>243</td>
<td>0.0555</td>
<td>HOMO-4 → LUMO+3</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>40.3</td>
<td>289</td>
<td>0.1577</td>
<td>HOMO-5 → LUMO</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>342</td>
<td>5.2</td>
<td>342</td>
<td>0.0519</td>
<td>HOMO-3 → LUMO+1</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>2.9</td>
<td>376</td>
<td>0.0249</td>
<td>HOMO-1 → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>404</td>
<td>2.4</td>
<td>404</td>
<td>0.0284</td>
<td>HOMO → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>234</td>
<td>43.9</td>
<td>254</td>
<td>0.0603</td>
<td>HOMO-9 → LUMO</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>27.8</td>
<td>287</td>
<td>0.1571</td>
<td>HOMO-3 → LUMO+1</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>340</td>
<td>4.8</td>
<td>341</td>
<td>0.0335</td>
<td>HOMO-2 → LUMO</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>376</td>
<td>2.6</td>
<td>377</td>
<td>0.0259</td>
<td>HOMO-1 → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>404</td>
<td>2.1</td>
<td>405</td>
<td>0.0284</td>
<td>HOMO → LUMO</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>0.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Electrochemical and DFT MO Energy Data for Complexes 5–8

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{\text{ox}}$ (V)$^a$</th>
<th>$E_{\text{red}}$ (V)$^a$</th>
<th>$E_{\text{ox}} - E_{\text{red}}$ (V)</th>
<th>HOMO (eV)$^b$</th>
<th>LUMO (eV)$^b$</th>
<th>HLG (eV)$^{bc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.26</td>
<td>-2.94</td>
<td>3.20</td>
<td>-4.86</td>
<td>-1.10</td>
<td>3.76</td>
</tr>
<tr>
<td>6</td>
<td>0.41</td>
<td>-2.94</td>
<td>3.35</td>
<td>-4.97</td>
<td>-1.16</td>
<td>3.81</td>
</tr>
<tr>
<td>7</td>
<td>0.23</td>
<td>-3.02</td>
<td>3.25</td>
<td>-4.84</td>
<td>-1.05</td>
<td>3.79</td>
</tr>
<tr>
<td>8</td>
<td>0.23</td>
<td>-3.02</td>
<td>3.25</td>
<td>-4.84</td>
<td>-1.06</td>
<td>3.78</td>
</tr>
</tbody>
</table>

$^a$Measured in degassed acetonitrile solution (10$^{-3}$ M) / [Bu$_4$N]PF$_6$ (0.1 M), vs Fc/Fc$^+$ at 0.1 V s$^{-1}$, at room temperature. $^b$Values from electronic structure DFT calculations. $^c$HLG = LUMO – HOMO.

Complexes 5–8 are emissive in the blue-green spectral region upon photoexcitation, in doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in powder at room temperature and in 2-methyltetrahydrofuran at room temperature and 77 K, displaying bands centered between 455 and 520 nm. Figure 3 depicts the emission spectra, whereas Table 3 summarizes calculated and experimental wavelengths, lifetimes, quantum yields at room temperature in PMMA films and 2-methyltetrahydrofuran solutions, and radiative and nonradiative rate constants. The emission spectra in PMMA films, in neat solid powders, and in 2-methyltetrahydrofuran at room temperature show broad structureless bands. However, the spectra in glassy 2-methyltetrahydrofuran, at 77 K, display vibronic fine structures which are consistent with a notable contribution of ligand centered $^3\pi-\pi^*$ transitions to the excited state. The emission maxima further undergo a blue shift, which has been attributed to a significant additional $^3$MLCT character of the excited state at room temperature.$^{7d,22}$ The nature of the substituents of the cyclometalated phenylpyridine has a moderated influence on the emission. Thus, while the methyl substituted complexes 7 and 8 display emission wavelengths similar to the unsubstituted derivative 5, the emission wavelength of the fluoride disubstituted compound 6 undergoes a
higher energy shift of about 30 nm. This blue shift is in agreement with the higher HOMO-LUMO gap of 6 with regard to those of 5, 7, and 8. It should be noted that although the reduction potentials of the four complexes are similar, the oxidation potential of 6 is higher. The lifetimes are short lying in the range 0.6–4.8 μs, whereas the quantum yields, measured in PMMA films are in all cases close to the unity (0.87–0.96), whereas are approximately 1 for 5, 7, and 8 and 0.73 for 6 in solution at room temperature. In this context, it should be mentioned that, as far as we know, the highest quantum yield reported for complexes with two free cyclometalated aryl-NHC ligands is 0.79.7e In PMMA films, the radiative rate constants are one order of magnitude higher than the nonradiative rate constants for 5, 7, and 8 whereas are of the same order of magnitude for 6. The radiative rate constants in PMMA films and solution are comparable. The exceptional quantum yields in solution suggest that the rigidity of the structure imposed by the linker between the carbene moieties plays a main role in the brightness of the emitters.
Figure 3. Emission spectra in 5 wt% PMMA films at 298 K (a), in neat solid powders at 298 K (b), in MeTHF at 298K (c), and in MeTHF at 77 K (d) for complexes 5–8.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Calcd λ&lt;sub&gt;em&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (nm)</th>
<th>Media (T/K)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;exc&lt;/sub&gt; (nm)</th>
<th>τ (μs)</th>
<th>Φ</th>
<th>k&lt;sub&gt;r&lt;/sub&gt; (s&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>k&lt;sub&gt;n&lt;/sub&gt;&lt;sub&gt;r&lt;/sub&gt; (s&lt;sup&gt;-1&lt;/sup&gt;)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>k&lt;sub&gt;r&lt;/sub&gt;/k&lt;sub&gt;n&lt;/sub&gt;&lt;sub&gt;r&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>PMMA film (298)</td>
<td>509</td>
<td>407</td>
<td>1.7</td>
<td>0.93</td>
<td>5.5 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>4.1 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>powder (298)</td>
<td>519</td>
<td>475</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (298)</td>
<td>510</td>
<td>431</td>
<td>3.9</td>
<td>~1</td>
<td>2.6 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (77)</td>
<td>478, 506</td>
<td>439</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>PMMA film (298)</td>
<td>485</td>
<td>401</td>
<td>1.3</td>
<td>0.87</td>
<td>6.7 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.0 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>6.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>powder (298)</td>
<td>485</td>
<td>450</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (298)</td>
<td>473</td>
<td>394</td>
<td>1.6</td>
<td>0.73</td>
<td>4.6 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>1.7 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (77)</td>
<td>455, 484</td>
<td>396</td>
<td>3.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>PMMA film (298)</td>
<td>509</td>
<td>401</td>
<td>1.7</td>
<td>0.93</td>
<td>5.5 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>4.1 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>powder (298)</td>
<td>517</td>
<td>470</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (298)</td>
<td>492</td>
<td>424</td>
<td>3.1</td>
<td>~1</td>
<td>3.2 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (77)</td>
<td>473, 506</td>
<td>429</td>
<td>4.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PMMA film (298)</td>
<td>508</td>
<td>403</td>
<td>1.8</td>
<td>0.96</td>
<td>5.3 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>2.2 x 10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>24.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>powder (298)</td>
<td>513</td>
<td>475</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (298)</td>
<td>492</td>
<td>425</td>
<td>2.4</td>
<td>~1</td>
<td>4.2 x 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeTHF (77)</td>
<td>476, 510</td>
<td>429</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Predicted from TD-DFT calculations in THF at 298 K. <sup>b</sup>CALCULATED according to the equations \( k_r = \phi / \tau \) and \( k_{n\text{r}} = (1 - \phi) / \tau \), where \( k_r \) is the radiative rate constant, \( k_{n\text{r}} \) is the nonradiative rate constant, \( \phi \) is the quantum yield, and \( \tau \) is the excited-state lifetime.
The emissions can be attributed to T\textsubscript{1} excited states originated by HOMO→LUMO charge transfer transitions. Figure 4 displays the spin density distribution calculated for the T\textsubscript{1} states at their minimum energy geometry. In accordance with this, good agreement is observed between the experimental wavelengths and those calculated by estimating the difference in energy between the optimized triplet state and the singlet state S\textsubscript{0}, in tetrahydrofuran.

![Image](https://example.com/image.png)

**Figure 4.** Unpaired electron spin-contours density (0.03 au) calculated for the T\textsubscript{1} states of complexes 5–8.

**CONCLUDING REMARKS**

This study shows the discovery of a family of iridium(III) emitters of the class [6tt+3b], which contain a C,C,C,C-tetradentate ligand and display quantum yields close to the unity. In addition, the study reveals that there are marked differences in stereochemistry and photophysical features between the compounds with two free cyclometalated aryl-NHC ligands and those bearing the NHC moieties linked by a butylene chain.
The coordination mode of bis(N-phenyl)-bis(NHC) ligands depends upon the metal precursor. In contrast to the pentahydride IrH₅(PPh₃)₂, that reacts with 1,1-diphenyl-3,3-butylenediimidazolium iodide to afford a bis(NHC) bridge, the known dimer [Ir(μ-OMe)(COD)]₂ metalates the cation of this salt to generate a C,C,C,C,C-tetradentate ligand, formed by two cyclometalated Ph-NHC moieties linked by a butylene chain, which coordinates to only one iridium atom. The resulting species is easily transformed into the cation [Ir{κ⁴-C,C,C,C-[C₆H₄Im(CH₂)₄ImC₆H₄]}(CH₃CN)₂]⁺, which promotes the pyridyl supported heterolytic ortho-CH bond activation of the phenyl group of phenylpyridines to give the [6tt+3b] complexes in almost quantitative yield. In contrast to the complexes with two free cyclometalated aryl-NHC ligands, the structures of these compounds have the NHC moieties of the tetradentate ligand disposed mutually cis. The rigidity imposed by the chain not only changes the disposition of the donor atoms in the coordination sphere of the metal, but also produces an increase of the quantum efficiency. Thus, they are blue-green emitters, which display short lifetimes (0.6–4.8 μs) and reach quantum yields close to the unity, upon photoexcitation, in both doped poly(methylmethacrylate) (PMMA) films at 5 wt% and in 2-methyltetrahydrofuran at room temperature.

In conclusion, the linkage of chelate ligands with alkylene chains allows to stabilize particular isomers of heteroleptic iridium(III) emitters, containing three bidentate units, and reduces the mixtures due to ligand redistribution. Furthermore, the rigidity imposed by the chain increases the quantum efficiency.

**EXPERIMENTAL SECTION**

Reactions were performed under argon with dried solvents using Schlenk-tube techniques. Instrumental methods used for characterization, X-ray information, and DFT computational details are given in the Supporting Information. Chemical shifts (in ppm) are referenced to
residual solvent peaks (\(^1\)H, \(^{13}\)C\(^{\{1\}H}\)) or external CFCl\(^3\) (\(^{19}\)F) whereas coupling constants \(J\) are given in hertz. Complex [Ir(\(\mu\)-OMe)(COD)]\(_2\) (I)\(^{23}\) and 1,1'-diphenyl-3,3'-butylenediimidazolium iodide\(^{24}\) were prepared according to the published methods.

**Preparation of [Ir(\(\mu\)-I)[\(\kappa^4\)-C,C,C,C-[C\(_6\)H\(_4\)Im(CH\(_2\)\(_4\)ImC\(_6\)H\(_4\)]]\(_2\) (2).** A mixture of 1 (213.2 mg, 0.322 mmol), 1,1'-diphenyl-3,3'-butylenediimidazolium iodide (654 mg, 1.09 mmol), and sodium tert-butoxide (154.5 mg, 1.61 mmol) in 15 mL of 2-methoxyethanol was heated at 130 °C in a Schlenk flask with a Teflon stopcock for 6 h. During this time a white solid appeared. The resulting suspension was transferred to a Schlenk flask. After cooling to room temperature, the white solid was decanted, washed with methanol (4 x 3 mL) and dried in vacuo. Yield: 276 mg (65%). Anal. Calcd for C\(_{44}\)H\(_{40}\)I\(_2\)Ir\(_2\)N\(_8\): C, 40.06; H, 3.06; N, 8.50. Found: C, 40.19; H, 3.39; N, 8.09. HRMS (electrospray, \(m/z\)): Calcd for C\(_{22}\)H\(_{20}\)IrN\(_4\) [M/2 – I]\(^+\): 533.1312; found 533.1312.

\(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 8.75 (m, 2H, Ph), 7.67 (d, 2H, \(^3\)J\(_{H-H}\) = 2.0, Im), 7.28 (d, 2H, \(^3\)J\(_{H-H}\) = 2.1, Im), 7.25 (m, 4H, Ph), 7.22 (d, 2H, \(^3\)J\(_{H-H}\) = 2.0, Im), 7.15 (m, 2H, Ph), 7.01 (dd, 2H, \(^3\)J\(_{H-H}\) = 7.7, \(^4\)J\(_{H-H}\) = 1.3, Ph), 6.68 (ddd, 2H, \(^3\)J\(_{H-H}\) = \(^3\)J\(_{H-H}\) = 7.4, \(^4\)J\(_{H-H}\) = 1.3, Ph), 6.55 (d, 2H, \(^3\)J\(_{H-H}\) = 2.1, Im), 6.56 (ddd, 2H, \(^3\)J\(_{H-H}\) = \(^3\)J\(_{H-H}\) = 7.4, \(^4\)J\(_{H-H}\) = 1.3, Ph), 6.18 (dd, 2H, \(^3\)J\(_{H-H}\) = 7.7, \(^4\)J\(_{H-H}\) = 1.3, Ph), 5.27, 3.61, 3.40, 2.44 (all m, 2H each, NCH\(_2\)), 2.13, 2.03, 1.93, 1.48 (all m, 2H each, NCH\(_2\)CH\(_2\)). \(^{13}\)C\(^{\{1\}H}\) NMR (100.63 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta\) 175.6, 153.0 (both IrC Im), 150.7 (IrC Ph), 147.7, 146.3 (both NC Ph), 141.3, 136.3 (both CH Ph), 131.7 (IrC Ph), 126.3, 124.4 (both CH Ph), 122.8 (CH Im), 121.9, 121.6 (both CH Ph), 120.5, 115.7, 114.4 (all CH Im), 111.3, 110.5 (both CH Ph), 51.8, 48.1 (both NCH\(_2\)), 29.4, 26.0 (both NCH\(_2\)CH\(_2\)).

**Preparation of [Ir(\(\kappa^4\)-C,C,C,C-[C\(_6\)H\(_4\)Im(CH\(_2\)\(_4\)ImC\(_6\)H\(_4\)]]\(_2\)(\(\mu\)-OH)(\(\mu\)-OMe)] (3).** A solution of silver trifluoromethanesulfonate (86.0 mg, 0.335 mmol) in 5 mL of acetone was added to a suspension of 2 (201.0 mg, 0.152 mmol) in dichloromethane (20 mL). The suspension was
stirred in the dark at room temperature, for 1 h. Then, it was filtered through Celite to remove the precipitated AgI. The solvent of the filtrate was almost removed in vacuo. The addition of diethyl ether (3 mL) caused the precipitation of a white solid that was dried in vacuo. The white solid was dissolved in MeOH (7 mL) and a solution of KOH (18.8 mg, 0.335 mmol) in MeOH (3 mL) was added to the previous one. After 2 hours at room temperature, a white solid was formed. It was decanted and washed with further portions of MeOH (3 x 3 mL). Yield: 80 mg (47%). Anal. Calcd for C_{45}H_{44}Ir_{2}N_{8}O_{2}: C, 48.55; H, 3.98; N, 10.06. Found: C, 48.31; H, 3.89; N, 9.99. HRMS (electrospray, \textit{m/z}): calcd for C_{22}H_{20}IrN_{4} [Ir\{C_{6}H_{4}Im(CH_{2})_{4}ImC_{6}H_{4}\}]^{+}: 533.1312; found 533.1394. ¹H NMR (400 MHz, CD_{2}Cl_{2}, 298 K): \delta 7.56 (d, 2H, 3\textit{J}_{H-H} = 2.0, \text{CH Im}), 7.47 (dd, 2H, 3\textit{J}_{H-H} = 7.1, 4\textit{J}_{H-H} = 1.4, \text{CH Ph}), 7.29 (d, 2H, 3\textit{J}_{H-H} = 2.1, \text{CH Im}), 7.14 (m, 2H, CH Ph), 7.08 (ddd, 2H, 3\textit{J}_{H-H} = 3\textit{J}_{H-H} = 7.4, 4\textit{J}_{H-H} = 1.4, \text{CH Ph}), 6.98 (dd, 2H, 3\textit{J}_{H-H} = 7.6, 4\textit{J}_{H-H} = 1.4, \text{CH Ph}), 6.89 (dd, 2H, 3\textit{J}_{H-H} = 7.1, 4\textit{J}_{H-H} = 1.4, \text{CH Ph}), 6.86 (d, 2H, 3\textit{J}_{H-H} = 2.0, \text{CH Im}), 6.65 (ddd, 2H, 3\textit{J}_{H-H} = 3\textit{J}_{H-H} = 7.4, 4\textit{J}_{H-H} = 1.3, \text{CH Ph}), 6.51 (d, 2H, 3\textit{J}_{H-H} = 2.1, \text{CH Im}), 6.30 (ddd, 2H, 3\textit{J}_{H-H} = 3\textit{J}_{H-H} = 7.4, 4\textit{J}_{H-H} = 1.5, \text{CH Ph}), 3.45, 3.29, 3.02 (all m, 2H each, NCH_{2}), 2.48 (s, 3H, OCH_{3}), 2.38 (m, 2H, NCH_{2}CH_{2}), 2.16 (m, 2H, NCH_{2}), 1.75, 1.64, 1.24 (all m, 2H each, NCH_{2}CH_{2}), –0.77 (s, 1H, OH). ¹³C\{¹H\} NMR (100.63 MHz, CD_{2}Cl_{2}, 298 K): \delta 182.7, 160.9 (both IrC Im), 156.8 (IrC Ph), 148.8, 148.4 (both NC Ph), 139.4, 137.7 (both, CH Ph), 133.0 (IrC Ph), 124.2, 123.7 (both CH Ph), 123.1 (CH Im), 121.0, 120.6 (both, CH Ph), 120.2, 114.6, 114.4 (all CH Im), 110.4, 109.4 (both CH Ph), 57.3 (s, OCH_{3}), 49.0, 47.7 (both NCH_{2}), 29.8, 21.9 (both, NCH_{2}CH_{2}).

**Preparation of [Ir(κ⁴-C,C,C,C-[C₆H₄Im(CH₂)₄ImC₆H₄])(CH₃CN)]₂[OTf] (4)** A solution of silver trifluoromethanesulfonate (87.6 mg, 0.341 mmol) in 5 mL of acetone was added to a suspension of 2 (204.5 mg, 0.155 mmol) in dichloromethane (20 mL). The suspension was
stirred in the dark at room temperature, for 1 h. Then, it was filtered through Celite to remove the precipitated AgI. The solvent of the filtrate was almost removed in vacuo. The addition of diethyl ether (3 mL) caused the precipitation of a white solid that was dried in vacuo. The solid was dissolved in acetonitrile (5 mL) forming a colorless solution. The solvent was almost removed under reduced pressure and the addition of diethyl ether (3 mL) caused the precipitation of a white solid that was washed with further portions of diethyl ether (3 x 3 mL). Yield: 168 mg (71%). Anal. Calcd for C_{27}H_{26}F_3IrN_6O_3S: C, 42.45; H, 3.43; N, 11.00; S, 4.20. Found: C, 42.53; H, 3.65; N, 10.82; S, 4.55. HRMS (electrospray, m/z): calcd for C_{24}H_{23}IrN_5 [M - NCCH_3]^+ 574.1578; found 574.1662. IR (cm^{-1}): \nu(CN) 2260 (br, m), \nu(CF_3 + SO_3) 1250, 1222, 1148, 1027 (m). \textsuperscript{1}H NMR (400 MHz, CD_2Cl_2, 298 K): \delta 7.86 (m, 1H, Ph), 7.65 (d, 1H, \textit{J}_{H-H} = 2.0, Im), 7.37 (d, 1H, \textit{J}_{H-H} = 2.1, Im), 7.28 (d, 1H, \textit{J}_{H-H} = 2.0, Im), 7.23 (m, 3H, Ph), 7.11 (dd, 1H, \textit{J}_{H-H} = 7.6, \textit{J}_{H-H} = 1.3, Ph), 6.86 (ddd, 1H, J_{H-H} = 7.6, \textit{J}_{H-H} = 1.4, Ph), 6.74 (d, 1H, \textit{J}_{H-H} = 2.1, Im), 6.53 (ddd, 1H, J_{H-H} = 7.6, \textit{J}_{H-H} = 1.3, Ph), 6.34 (dd, 1H, \textit{J}_{H-H} = 7.6, \textit{J}_{H-H} = 1.4, Ph), 4.72, 4.33, 3.57 (all m, 1H each, NCH_2), 2.38 (m, 1H, NCH_2CH_2), 2.37, 2.32 (both s, 3H each, CH_3CN), 2.14 (m, 2H, NCH_2CH_2), 1.92, 1.81 (both m, 1H each, NCH_2CH_2). \textsuperscript{19}F NMR (282.33 MHz, CD_2Cl_2, 298 K): \delta -78.9 (s). \textsuperscript{13}C{\textsuperscript{1}H} NMR (100.63 MHz, CD_2Cl_2, 298 K): \delta 170.9, 151.1 (both IrC Im), 147.5, 147.3 (both NC Ph), 146.8 (IrC Ph), 137.9, 135.4, 126.5, 125.2 (all CH Ph), 124.6 (IrC Ph), 123.6, 123.5 (both CH Ph), 123.4, 122.0 (both CH Im), 120.1, 118.3 (both CH_3CN), 116.5, 115.2 (both CH Im), 111.8, 111.7 (both CH Ph), 51.8, 48.1 (both NCH_2), 30.1, 24.3 (both NCH_2CH_2), 4.3, 4.1 (both CH_3).

Preparation of \textit{Ir[\textit{C}_2\textit{C},\textit{C},\textit{C},\textit{C}-\textit{[C}_{6}\textit{H}_{4}\textit{Im}(\textit{CH}_{3})_{2}\textit{ImC}_{6}\textit{H}_{4})]}(\textit{\textit{C}_2\textit{C},\textit{N}-\textit{[C}_{6}\textit{H}_{4}-\textit{py})}) (5). A mixture of \textit{A} (268 mg, 0.351 mmol), (piperidinomethyl)polystyrene (100 mg, 0.351 mmol), and 2-phenylpyridine (50.1 \mu L, 0.351 mmol) was refluxed in 10 mL of fluorobenzene for 5h. After
cooling at room temperature, the resulting suspension was filtered through Celite. The oily residue remaining in the Schlenck flask was washed with dichloromethane (2 x 3 mL). The filtrate and washings were combined and the solvent removed under reduced pressure. The obtained yellow solid was washed with diethyl ether (3 x 3 mL). Yield: 193 mg (80%). Anal. Calcd for C₃₃H₂₈IrN₅: C, 57.71 H, 4.11; N, 10.20. Found: C, 57.49; H, 4.30; N, 9.84. HRMS (electrospray, m/z): calcd for C₃₃H₂₉IrN₅ [M + H]⁺ 688.2048; found 688.2042. ¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ 7.86 (d, 1H, 3 J_H-H = 8.0, py), 7.75 (dd, 1H, 3 J_H-H = 5.6, 4 J_H-H = 1.3, py), 7.69 (d, 1H, 3 J_H-H = 7.8, Ph), 7.58 (ddd, 1H, 3 J_H-H = 3 J_H-H = 8.0, 4 J_H-H = 1.3, py), 7.51 (d, 1H, 3 J_H-H = 1.9, Im), 7.41 (d, 1H, 3 J_H-H = 2.1, Im), 7.20 (d, 1H, 3 J_H-H = 7.4, Ph), 7.16 (d, 1H, 3 J_H-H = 7.3, Ph), 7.00-6.82 (m, 4H, Ph), 6.80 (d, 1H, 3 J_H-H = 1.9, Im), 6.78 (d, 1H, 3 J_H-H = 2.1, Im), 6.77-6.71 (m, 4H, 1H py + 3H Ph), 6.67 (ddd, 1H, 3 J_H-H = 3 J_H-H = 7.3, 4 J_H-H = 1.0, Ph), 6.38 (dd, 1H, 3 J_H-H = 7.3, 4 J_H-H = 1.0, Ph), 3.74 (m, 1H, NCH₂), 3.54 (m, 2H, NCH₂), 2.55 (m, 1H, NCH₂), 2.36 (m, 1H, NCH₂CH₃), 2.10 (m, 2H, NCH₂CH₃), 1.49 (m, 1H, NCH₂CH₂). ¹³C{¹H} NMR (75.47 MHz, CD₂Cl₂, 298 K): δ 176.7 (IrC Im), 172.2 (IrC Ph), 169.0 (NC py), 165.2 (IrC Im), 154.6, 153.7 (both IrC Ph), 151.0 (CH py), 148.6, 146.6, 145.0 (all C Ph), 139.54, 139.51 (both CH Ph), 135.6 (CH py), 132.8, 128.7, 125.7, 124.7, 124.2, 121.9 (all CH Ph), 121.5 (CH py), 120.7 (CH Im), 120.3 (CH Ph), 120.1 (CH Im), 119.7 (CH Ph), 118.9 (CH py), 116.3, 114.0 (both CH Im), 110.9, 110.4 (both CH Ph), 50.9, 47.9 both (NCH₂), 29.9, 26.4 (both NCH₂CH₃).

Preparation of Ir{κ⁴-C,C,C,C-[C₆H₄Im(CH₂)₄ImC₆H₄]}{κ²-C,N-[C₆H₂F₂-py]} (6). A mixture of 4 (220 mg, 0.288 mmol), (piperidinomethyl)polystyrene (82 mg, 0.288 mmol), and 2-(2,4-difluorophenyl)pyridine (45 µL, 0.288 mmol) was refluxed in 10 mL of fluorobenzene for 5h. After cooling at room temperature, the resulting suspension was filtered through Celite. The solvent was removed under reduced pressure and the addition of diethyl ether resulted on a
precipitation of a yellow solid that was washed with diethyl ether (3 x 3 mL). Yield: 170 mg (82%). Anal. Calcd for C33H26F2IrN5: C, 54.83 H, 3.63; N, 9.69. Found: C, 54.85 H, 3.54; N, 9.34. HRMS (electrospray, m/z): calcd for C33H27F2IrN5 [M + H]+ 724.1860; found 724.1897. 1H NMR (400 MHz, CD2Cl2, 298 K): δ 8.25 (dd, 1H, 3J_H-H = 8.0, 4J_H-H = 1.5, py), 7.82 (dd, 1H, 3J_H-H = 5.7, 4J_H-H = 1.0, py), 7.61 (dd, 1H, 3J_H-H = 8.0, 4J_H-H = 1.0, py), 7.52 (d, 1H, 3J_H-H = 2.0, Im), 7.41 (dd, 1H, 3J_H-H = 7.5, 4J_H-H = 1.3, Ph), 6.98 (ddd, 1H, 3J_H-H = 8.0, 4J_H-H = 1.0, py), 6.93 (dd, 1H, 3J_H-H = 7.5, 4J_H-H = 1.3, Ph), 6.82 (d, 1H, 3J_H-H = 7.5, 4J_H-H = 1.0, Im), 6.78-6.68 (m, 5H, 1H Im + 1H py + 3H Ph), 6.39 (dd, 1H, 3J_H-H = 7.2, 4J_H-H = 1.3, Ph), 6.32 (m, 2H, dfp), 3.72, 3.62, 3.54, 2.50 (all m, 1H each, NCH2), 2.24, 2.16, 2.07, 1.53 (all m, 1H each, NCH2CH2). 19F NMR (282.33 MHz, CD2Cl2, 298 K):  δ -111.14 (ddd, F2, 4J_F-F = 8.9, 5J_F-H = 2.4), -112.46 (ddd, F2, 4J_F-F = 8.9). T19F{1H} NMR (282.33 MHz, CD2Cl2, 298 K): δ -111.14 (d, F2, 4J_F-F = 8.9), -112.46 (d, F2, 4J_F-F = 8.9). 13C{1H} NMR (100.63 MHz, CD2Cl2, 298 K): δ 179.8 (dd, 3J_C-F = 2.9, 3J_C-F = 4.6, IrC dfp), 176.3 (s, IrC Im), 165.6 (d, 3J_C-F = 7.9, NC py), 164.3 (s, IrC Im), 163.4 (dd, 3J_C-F = 255.3, 3J_C-F = 10.8, CF), 162.6 (dd, 1J_C-C = 260.6, 3J_C-F = 11.5, CF), 153.6 (s, IrC Ph), 152.3 (dd, 3J_C-F = 2.2, IrC Ph trans to C6H2F2-py), 151.2 (s, CH py), 148.5, 146.6 (both s, C Ph), 139.3 (s, CH Ph), 136.2 (s, CH py), 133.0 (s, CH Ph), 128.7 (d, 3J_C-F = 2.5, C-py dfp), 126.0, 125.1 (both s, CH Ph), 123.0 (d, 2J_C-F = 22.5, CH py), 122.4 (s, CH Ph), 121.7 (s, CH py), 121.0 (s, CH Im), 120.9 (s, CH Ph), 120.6 (s, CH Im), 119.8 (dd, 2J_C-F = 13.6, 4J_C-F = 2.8, CH dfp), 116.7 (s, CH Im), 114.3 (s, CH Im), 111.2 (s, CH Ph), 110.9 (s, CH Ph), 95.8 (dd, 2J_C-F = 2J_C-F = 27.5, CH dfp), 51.3, 48.0 (both s, NCH2), 30.2, 26.5 (both s, NCH2CH2).

Preparation of Ir[k4-C6H4Im(CH2)4ImC6H4]{κ2-C,N-[C6H3Me-py]} (7). It was prepared following the procedure described for 6 starting from 4 (115 mg, 0.150 mmol), (piperidinomethyl)polystyrene (43 mg, 0.150 mmol), and 2-(p-tolyl)pyridine (25 μL, 0.150
mmol). Yellow solid. Yield: 95 mg (90%). Anal. Calcd for C34H30IrN5: C, 58.27 H, 4.31; N, 9.99. Found: C, 58.69 H, 4.17; N, 9.74. HRMS (electrospray, m/z): calcd for C34H30IrN5 [M + H]+ 702.2205; found 702.2212. 1H NMR (300 MHz, CD2Cl2, 298 K): δ 7.81 (d, 1H, 3JHH = 8.2, py), 7.72 (m, 1H, py), 7.58 (m, 1H, C6MeH3), 7.54 (m, 1H, py), 7.51 (d, 1H, 3JHH = 2.0, Im), 7.41 (d, 1H, 3JHH = 2.2, Im), 7.19 (m, 2H, Ph), 6.95 (m, 1H, Ph), 6.89 (m, 1H, Ph), 6.80 (d, 1H, 3JHH = 2.0, Im), 6.79 (d, 1H, 3JHH = 2.2, Im), 6.74-6.65 (m, 6H, 1H py + 3H Ph + 2H C6MeH3), 6.39 (dd, 1H, 3JHH = 7.2, 4JHH = 1.2, Ph), 3.75 (m, 1H, NCH2), 3.54 (m, 2H, NCH2), 2.57 (m, 1H, NCH2CH2), 2.38 (m, 1H, NCH2CH2), 2.13 (s, 3H, CH3), 2.07 (m, 2H, NCH2CH2), 1.47 (m, 1H, NCH2CH2). 13C{1H} NMR (75.48 MHz, CD2Cl2, 298 K): δ 176.9 (IrC Im), 172.2 (IrC C6H3Me), 169.1 (NC py), 165.4 (IrC Im), 154.9, 154.0 (both IrC Ph), 151.0 (CH py), 148.7, 146.8 (both CPh), 142.7 (C C6H3Me(-py)), 140.6 (CH C6H3Me), 139.6 (CH Ph), 138.4 (C C6H3Me(-CH3)), 135.6 (CH py), 133.0, 125.8, 124.8 (all CH Ph), 124.3 (CH C6H3Me), 122.0 (CH Ph), 121.2 (CH py), 121.1 (CH C6H3Me), 120.8 (CH Im), 120.3 (CH Ph), 120.2 (CH Im), 118.7 (CH py), 116.5, 114.1 (both CH Im), 111.0, 110.6 (both CH Ph), 50.9, 48.0 (both NCH2), 29.9, 26.7 (both NCH2CH2), 22.0 (CH3).

Preparation of Ir{κ4-C,C,C,C-[C6H4Im(CH2)4ImC6H4]}{κ2-C,C,N-[C6H3-Mepy]} (8). It was prepared following the procedure described for 6 starting from 4 (125 mg, 0.164 mmol), (piperidinomethyl)polystyrene (47 mg, 0.164 mmol), and 5-methyl-2-phenylpyridine (28 mg, 0.164 mmol). Yellow solid. Yield: 110 mg (95%). Anal. Calcd for C34H30IrN5: C, 58.27 H, 4.31; N, 9.99. Found: C, 58.48 H, 4.47; N, 9.72. HRMS (electrospray, m/z): calcd for C34H30IrN5 [M + H]+ 702.2205; found 702.2203. 1H NMR (400 MHz, CD2Cl2, 298 K): δ 7.75 (d, 1H, 3JHH = 8.3, py), 7.64 (d, 1H, 3JHH = 7.8, Ph), 7.53 (d, 1H, 4JHH = 0.9, NCH py), 7.53 (d, 1H, 3JHH = 2.0, Im), 7.42 (dd, 1H, 3JHH = 8.3, 4JHH = 0.9, py), 7.40 (d, 1H, 3JHH = 2.1, Im), 7.20 (d, 1H, 3JHH = 7.8,
Ph), 7.17 (d, 1H, \textit{J}_{H-H} = 7.3, Ph), 6.97 (m, 1H, Ph), 6.89 (ddd, 1H, \textit{J}_{H-H} = \textit{J}_{H-H} = 7.5, \textit{J}_{H-H} = 1.3, Ph), 6.86-6.81 (m, 2H, Ph), 6.80 (d, 1H, \textit{J}_{H-H} = 2.0, Im), 6.77 (d, 1H, \textit{J}_{H-H} = 2.1, Im), 6.77-6.72 (m, 3H, Ph), 6.67 (ddd, 1H, \textit{J}_{H-H} = \textit{J}_{H-H} = 7.2, \textit{J}_{H-H} = 1.0, Ph), 6.39 (dd, 1H, \textit{J}_{H-H} = 7.2, \textit{J}_{H-H} = 1.0, Ph), 3.75 (m, 1H, NCH\textsubscript{2}), 3.54 (m, 2H, NCH\textsubscript{2}), 2.56 (m, 1H, NCH\textsubscript{2}), 2.34 (m, 1H, NCH\textsubscript{2}CH\textsubscript{2}), 2.10 (m, 2H, NCH\textsubscript{2}CH\textsubscript{2}), 2.02 (s, 3H, CH\textsubscript{3}), 1.50 (m, 1H, NCH\textsubscript{2}CH\textsubscript{2}). \textsuperscript{13}C\{\textsuperscript{1}H\} NMR (100 MHz, CD\textsubscript{2}Cl\textsubscript{2}, 298 K): \textit{\delta} 176.8 (IrC Im), 171.2 (IrC Ph), 166.5 (NC py), 165.4 (IrC Im), 155.0, 153.9 (both IrC Ph), 151.0 (CHN py), 148.6, 146.7, 145.3 (all C Ph), 139.6, 139.5 (both CH Ph), 136.6 (CH py), 133.0 (CH Ph), 131.3 (CCH\textsubscript{2}), 128.5, 125.9, 124.8, 123.9, 122.0 (all CH Ph), 120.8, 120.4 (both CH Im), 119.8 (CH Ph), 118.5 (CH py), 116.5, 114.1 (both CH Im), 110.5 (CH Ph), 51.0, 48.0 (both NCH\textsubscript{2}), 30.1, 26.5 (both NCH\textsubscript{2}CH\textsubscript{2}), 18.5 (CH\textsubscript{3}).

**ASSOCIATED CONTENT**

**Supporting Information.** The following files are available free of charge.

General information, crystallographic data for complexes 3 and 5, computational details, \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} APT NMR of the complexes 2–8, experimental and computed UV/vis spectra, frontier molecular orbitals, cyclic voltammograms, and normalized excitation and emission spectra for complexes 5–8 (PDF)

Cartesian coordinates of compounds 5–8 (XYZ)

**Accession Codes**

CCDC 1580312 (3) and 1580313 (5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
AUTHOR INFORMATION

Corresponding Author

*E-mail: maester@unizar.es.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT

Financial support from the Spanish MINECO (Projects CTQ2017-82935-P, Red de Excelencia Consolider CTQ2016-81797-REDC), Gobierno de Aragón (E35), FEDER, and the European Social Fund (FSE) is acknowledged.

REFERENCES


(2) 3 is the number of electrons donated by the ligands, whereas b and b′ indicate the denticity of the ligands (bidentate). See: Esteruelas, M. A.; Oñate, E.; Palacios, A. U. Selective Synthesis and Photophysical Properties of Phosphorescent Heteroleptic Iridium(III) Complexes with Two Different Bidentate Groups and Two Different Monodentate Ligands. Organometalics 2017, 36, 1743–1755.


SYNOPSIS: Binding of a bis(aryl-N-heterocyclic carbene) as a tetradentate ligand to iridium(III) combined with a cyclometalated phenylpyridine ligand leads to complexes that are highly efficient blue-green emitters with quantum yields close to the unity.

For Table of Contents Only

\[ \Phi = 0.96 \]