

Encapsulated-Type Iridium(III) Phosphorescent Emitters with a Hexadentate Ligand of Three Different Bidentate Units

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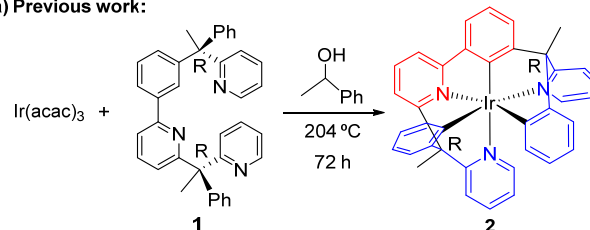
ABSTRACT: The preparation and photophysical properties of new phosphorescent iridium(III) emitters are reported. The metal center is encapsulated by a hexadentate ligand made up of three different bidentate fragments: orthometalated 2-phenylpyridine, orthometalated 2-benzylpyridine, and metalated 2-ethylpyridine. Their formation involves activation reactions of C(sp³)-H and C(sp³)-H bonds, assisted by pyridyl groups.

Phosphorescent iridium(III) emitters are at the forefront of photophysics¹ and photochemistry.² Among them, complexes with three different bidentate ligands, donors of 3 electrons each (3b), are the best option to generate emitters for a specific function, since they allow the finest adjustment of the photophysical characteristics that are intended to be achieved. However, the preparation of these heteroleptic species [3b+3b'+3b''] is difficult due to isomerization problems related to the existence of different stereoisomers and the ligand distribution equilibria experienced by these compounds.³ A possible solution to these issues is to join the 3b ligands by means of linkers, to form more rigid structures, maintaining the relative arrangement of the donor atoms in the coordination sphere of the iridium(III) center. A first approximation to the solution consisted of connecting two of the 3b ligands. This idea led to the design of interesting tetradentate ligands, donors of 6 electrons, with two different bidentate fractions (6tt'). Although a few [6tt'+3b] emitters were achieved, which partially mitigate the stereoisomers problem,⁴ the number of donor atom arrangements around the metal center that can be generated is still too high.⁵ One step further is to tie the three different bidentate ligands, binding each donor unit of one of them, 3b for example, with the other two, 3b' and 3b'', to form a rigid hexadentate ligand, donor of 9 electrons (9h), with three different bidentate moieties. In accordance with this approach, we recently designed and prepared proligand **1**; it can be seen as a 2-phenylpyridine joined via the phenyl and pyridyl units to the methylene group of two benzylpyridines, which bear a methyl substituent on the benzylic carbon atom. This molecule was subsequently used to generate compound **2**.⁶ The iridium(III) center of this emitter is encapsulated by the orthometalated moieties derived from the fragments 2-phenylpyridine and 2-benzylpyridine.⁷ Thus, complex **2** represents the first encapsulated emitter, formally tris-heteroleptic since the 2-benzylpyridine fragments are formally different because they are attached to different groups, phenyl and pyridyl, although it

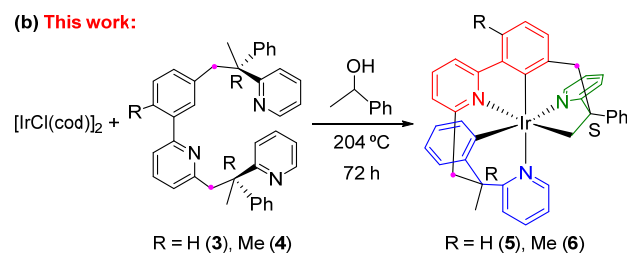
is actually a model of bis-heteroleptic emitter of the class [3b+3b+3b'] (Scheme 1a).⁸

Scheme 1. Preparation of Encapsulated-Type Iridium(III) Complexes Bearing a Hexadentate Ligand with Two and Three Different Bidentate Units^a

(a) Previous work:



(b) This work:



^a *S,S*-enantiomer of **1** affords *S,S*-enantiomer of **2**, whereas *S,S*-enantiomers of **3** and **4** lead to *S,R*-enantiomers of **5** and **6**.

The transformation of proligand **1** into the 9h ligand of **2** involves the coordination of the heteroatoms and the activation of an *ortho*-CH bond of the phenyl groups. We have now discovered that the insertion of a CH₂ unit between the 2-phenylpyridine moiety and the benzylic carbon atom of the 2-benzylpyridine moieties causes asymmetry in the C-H bond activation process; the 2-benzylpyridine moiety, attached to the phenyl unit of 2-phenylpyridine, undergoes C(sp³)-H bond activation of the methyl substituent, on the benzylic carbon atom, instead

of C(sp²)-H activation of the phenyl group observed for **1**. As a result, the C-H bond activation process leads to a true tris-heteroleptic emitter in which the metal ion is encapsulated by an hexadentate ligand made up of three really different bidentate fragments, namely: orthometalated 2-phenylpyridine, orthometalated 2-benzylpyridine, and metalated 2-ethylpyridine (Scheme 1b).

The introduction of the CH₂ units into the proligand **1** gives rise to proligand **3**. The new organic molecule was prepared by a Suzuki-Miyaura cross-coupling⁹ between 2-bromo-6-(2-phenyl-2-(2-pyridin-2-yl)propyl)pyridine and 2-(2-phenyl-1-(3-pinacoliborylphenyl)propan-2-yl)pyridine, using Pd(PPh₃)₄ as catalyst precursor and Cs₂CO₃ as base. The utilization of a reagent with a methyl substituent on the 4-position of the borylated phenyl group similarly provides the analogous methylated proligand **4**. These molecules, which were obtained as racemates of the *RR/SS* and *RS/SR* diastereomers, were transformed into the 9h ligands of the respective emitters **5** (R = H) and **6** (R = Me) by reaction with the well-known dimer [Ir(μ -Cl)(COD)]₂ (COD = 1,5-cyclooctadiene), in 1-phenylethanol, at reflux, for 72 h, as shown in Scheme 1b. Complexes **5** and **6** are unusual examples of iridium derivatives stabilized by six-coordinate ligands bearing σ -donor C atoms. We note that the few reported iridium(III) complexes of this class are based on tripodal structures, containing flexible arms attached to the phenyl or pyridyl units of three orthometalated 2-phenylpyridines.¹⁰ Therefore, they are much more flexible than our 9h ligands and also have a homo-leptic nature, in contrast to **5** and **6**. Molecular structure of **5** as determined by single-crystal X-ray diffraction (SC-XRD) (Figure 1) demonstrates the encapsulated nature of these novel complexes, showing a *fac*-arrangement of nitrogen and carbon atoms in an octahedral environment around the iridium(III) center. It is worth highlighting the *trans*-N-Ir-C angles, 167–175°, due to their closeness to the ideal value of 180°. Such proximity suggests high molecular stability. Indeed, DFT calculations (B3LYP-D3//SDD(f)-6-31G**) reveal that **5** is the most stable racemate of the sixteen diastereomers that can be generated in the process of N-coordination and activation of C-H bonds of proligand **3**, promoted by the dimer [Ir(μ -Cl)(COD)]₂ (see Chart S1).¹¹ According to the configuration of the asymmetric carbon atoms of **5**, it should also be noted that only the *SS/RR* racemates, of the mixtures of diastereoisomers that form **3** and **4**, work to achieve the emitters. The C(sp³)-H bond activation of the respective racemate of proligands **3** and **4**, in the presence of an unreactive phenyl group, is also supported by the ¹³C{¹H} NMR spectra of **5** and **6**, in dichloromethane-*d*₂. As Figures S6 and S8 show, they contain a singlet at about 36 ppm that corresponds to the metalated C(sp³) atom.

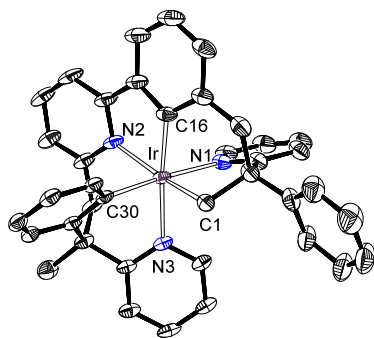


Figure 1. Molecular structure of **5** as determined by SC-XRD. Selected bond lengths (Å) and angles (deg): Ir-C(1) = 2.054(5), Ir-C(16) = 2.018(5), Ir-C(30) = 2.016(4), Ir-N(1) = 2.100(4), Ir-N(2) = 2.172(4), Ir-N(3) = 2.183(4); N(1)-Ir-C(30) = 174.26(16), N(2)-Ir-C(1) = 167.01(16), N(3)-Ir(1)-C(16) = 174.81(17).

The UV-vis spectra of **5** and **6**, in 2-methyltetrahydrofuran (2-MeTHF) solutions, at room temperature display bands with intensity that depend on the spectrum region (Figure S9). The most intense absorptions ($\epsilon \approx 20000$ – 14000 M⁻¹ cm⁻¹) are observed below 300 nm, whereas bands of intermediate intensity ($\epsilon \approx 6000$ – 2000 M⁻¹ cm⁻¹) appear between 350 and 430 nm. The weakest absorptions ($\epsilon < 2000$ M⁻¹ cm⁻¹) are discerned at energy below 450 nm. Spectra were calculated and bands assigned based on TD-DFT calculations (B3LYP-D3//SDD(f)-6-31G**) in tetrahydrofuran (Figure S10; Tables S1-S2). Higher energy bands are due to intraligand ¹ π - π^* transitions. Absorptions in the region 350–430 nm correspond to spin allowed charge transfers from the iridium center to the heterocycles combined with transitions from the orthometalated phenyl groups to the heterocycles. The tails after 450 nm imply formal spin-forbidden HOMO-LUMO transitions, which result from large spin-orbit coupling provided by the 5d metal. The HOMO of both compounds is distributed over the metal center ($\approx 50\%$) and the metalated phenyl groups, while the LUMO is delocalized over the heterocycles (Figures S11 and S12 and Tables S3 and S4). The DFT calculated HOMO energy levels agree with those obtained from an electrochemical study (-4.79 *versus* -4.95 (**5**) and -4.76 *versus* -4.93 (**6**) eV).¹² Voltammograms (Figure S13) were recorded in acetonitrile, under argon, using [Bu₄N]PF₆ as supporting electrolyte (0.1 M). They show a quasi-reversible oxidation from Ir(III) to Ir(IV) at potentials, against Fc/Fc⁺, of 0.15 (**5**) and 0.13 (**6**) V, which compare well with that measured for the oxidation of **2** (0.14 V).⁶ Reductions were not observed in the range of the solvent window.

Emissive properties of **5** and **6** were studied in doped poly(methyl methacrylate) films at 5 wt% (PMMA), at room temperature, and in 2-methyltetrahydrofuran at room temperature and at 77 K. Upon photoexcitation, both compounds emit in the green region of the visible spectrum (554–514 nm) (Figure S28). Emissions come from the respective excited state T₁, as supported by the excellent agreement between the wavelengths of the maxima and the calculated values for the energy differences between the optimized T₁ and singlet ground state S₀, in tetrahydrofuran. The shape of the bands is almost identical in both compounds, with fwhm values in the range 60–95 nm. The lifetimes are short (0.2–7.6 μ s), whereas the quantum yields in PMMA (0.41–0.44) are similar to that of **2** (0.41). However, in contrast to the latter, they fall to 0.07–0.03 in MeTHF (Table 1). This appears to be due to the rise of the nonradiative rate constants (k_{nr}), in solution, which are about an order of magnitude higher than in PMMA. The same behavior has been observed for the [6tt'+3b] complexes, Ir{ κ^4 -N,C,C',O-[py-MeC₆H₃-C(CH₂-C₆H₄)NHC(R)O]}{ κ^2 -C,N-(MeC₆H₃-py)} (R = Ph, Me), which also have an Ir-C(sp³) bond.¹³

We can conclude that joining the bidentate ligands of tris-heteroleptic phosphorescent iridium(III) complexes, to generate encapsulated-type related emitters with three different bidentate fragments, is a promising approach to prevent isomerization problems and distribution equilibria of ligands. There is certainly work to be done on the design of precursor molecules for the hexadentate ligands and how to coordinate them to the

metal, but the results of the first attempts in this direction are evidently more than satisfactory.

Table 1. Emission Data for 5 and 6

Complex	calcd λ_{em}^a (nm)	media (T/K)	λ_{em} (nm)	τ (μ s)	Φ	k_r^b (s^{-1})	k_{nr}^b (s^{-1})	k_r/k_{nr}
5	522	PMMA (298)	539	1.0	0.41	4.1×10^5	5.9×10^5	0.7
		2-MeTHF (298)	535	0.2	0.03	1.5×10^5	4.9×10^6	0.03
		2-MeTHF (77)	514, 551	7.6				
6	518	PMMA (298)	553	1.4	0.44	3.1×10^5	4.0×10^5	0.7
		2-MeTHF (298)	548	0.5	0.07	1.4×10^5	1.9×10^6	0.07
		2-MeTHF (77)	523, 554	5.3				

^aPredicted from TD-DFT calculations in THF at 298 K. ^b $k_r = \phi/\tau$ and $k_{nr} = (1 - \phi)/\tau$. ϕ is the quantum yield, and τ is the excited-state lifetime.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental section, structural analysis, computational details and energies of optimized structures, experimental and computed UV/vis spectra, cyclic voltammograms, molecular orbitals, normalized excitation and emission spectra, and NMR spectra. (PDF)

Cartesian coordinates of the optimized structures (XYZ)

Accession Codes

CCDC 2245722 contain 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.

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Notes

The authors declare no competing financial interest.

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- (11) The C(sp³)–H activation of the methyl substituent on the benzylic carbon atom of one of the benzylpyridine moieties of **1** could afford eight different diastereoisomers, which are between 9.6 and 27.1 kcal mol^{−1} less stable than **2**.
- (12) Experimental HOMO energy level = $-[E_{1/2}^{ox} \text{ vs } Fc/Fc^+ + 4.8]$ eV. See: Cardona, C. M.; Li, W.; Kaifer, A. E.; Stockdale, D.; Bazan, G. C. Electrochemical Considerations for Determining Absolute Frontier Orbital Energy Levels of Conjugated Polymers for Solar Cell Applications. *Adv. Mater.* **2011**, *23*, 2367–2371.
- (13) Benítez, M.; Buil, M. L.; Esteruelas, M. A.; Izquierdo, S.; Oñate, E.; Tsai, J.-Y. Acetylides for the Preparation of Phosphorescent Iridium(III) Complexes: Iridaoxazoles and Their Transformation into Hydroxycarbenes and *N,C(sp³),C(sp²),O*-Tetradentate Ligands. *Inorg. Chem.* **2022**, *61*, 19597–19611.

TOC Graphic.

