Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence

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Abstract: A fused π-helical N-heterocyclic (NHC) system was prepared and examined through its diastereoisomerically pure cycloiridiated complexes. The latter display light-green phosphorescence with unusually long lifetimes and circular polarization that depends on both the helical-NHC *P*/*M* and the iridium *Δ*/*Λ* stereochemistry. These unprecedented features are attributed to extended π-conjugation within helical carbenic ligand and efficient helicene-NHC-Ir interaction.

Octahedral cyclometalated iridium(III) complexes[1] have attracted attention due to their applications as phosphors in organic light-emitting devices (OLEDs),[2] and for their biological activity.[3] To date, several classes of enantiopure cycloiridiated systems have been reported.[1b,4] As for Ir(III) complexes bearing N-heterocyclic carbene (NHC) ligands, while few examples have been shown to display deep blue phosphorescence (a challenging target in the OLED area[5,6]), *chiral* NHC-based systems for molecular materials science are almost unknown. Furthermore, no chiral purely π-helical NHC has been reported to date.[7,8] Herein, we describe the synthesis of a π-conjugated *ortho*-fused [5]helicenic NHC ligand (in which an NHC is incorporated within a helical core) through its diastereoisomerically pure cycloiridiated complexes $A^{1,2}$ (Figure 1). We detail their electronic and structural features, stereochemistry, photophysical and chiroptical properties experimentally and computationally.

Scheme 1 shows the strategy to prepare the [5]helicene-imidazolium iodide salt (±)-**5**. First, the [5]helicene-thiadiazole **1**[9a] was reduced to 1,2-diamino-[4]helicene **2** with $LiAlH_4$,[9b] which was then directly cyclized to the precarbenic [5]helical imidazole **3** using triethyl orthoformate in the presence of catalytic iodine in acetonitrile.[9c] To our knowledge **3** is the first fully *π-helicenic imidazole* since it displays five *ortho*-fused aromatic rings including the terminal imidazole cycle.

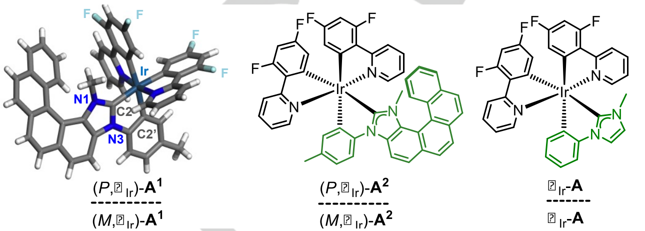
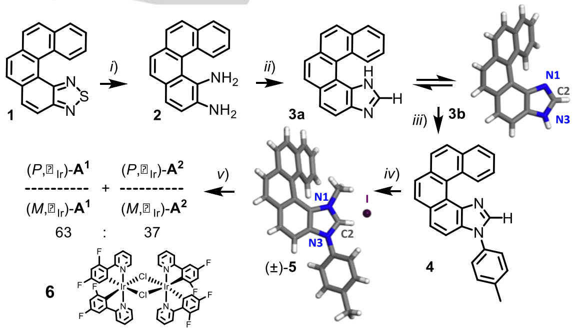


Figure 1. Meridional cycloiridiated complexes $A^{1,2}$ bearing a *P*-[5]helicene-NHC chelating ligand (in grey) and model NHC complex **A** lacking the helicene unit.[5c] X-ray structure of A^1 ((*P*,*Λ*Ir) enantiomer shown).



Scheme 1. Preparation of [5]helicene-imidazolium salt (±)-**5** and of cycloiridiated complexes $A^{1,2}$. *i*) $LiAlH_4$, THF, Ar, r.t., 5 hrs; *ii*) $HC(OEt)_3$, cat. I_2, CH_3CN, r.t. 2 hrs, 52% (two steps); *iii*) *p*-tolyl-boronic acid, anhydrous $Cu(OAc)_2$, pyridine, CH_2Cl_2, air, molecular sieves, r.t., 24 hrs, 69%; *iv*) CH_3I, CH_3CN, reflux, 18 hrs, 91%.; *v*) **6**, Ag_2O (2 eq.), 1,2-dichloroethane, 90°C, 16 hrs, dark, 76%. X-ray structures of tautomer (±)-**3b** and of (±)-**5** (*P* enantiomers shown).

Two tautomeric forms[10a] (**3a**,**b** in Scheme 1) are seen by ^1H NMR spectroscopy (Figure S2 in SI) and are in exchange at 75°C on the NMR timescale. X-ray crystallography ascertained the helical nature of **3**, which crystallized as its **3b** tautomer in the *Ia* centro-symmetric space group, with both *P* and *M* enantiomers (Scheme 1, SI). The imidazole ring reveals classical metric data (C2–N1 (C2–N3) bond-length: 1.320 (1.345) Å),[10b] while the molecule shows a helicity (dihedral angle between the terminal rings) of 42.27°. A Chan-Lam coupling[11] of **3** with *p*-tolyl-boronic acid furnished **4**, whose methylation with CH_3I in excess gave the imidazolium salt (±)-**5**. While the [5]helicenic imidazole derivatives **3** and **4** are configurationally unstable in solution (the enantiomers could not be resolved by chiral HPLC at 10°C, which indicates an inversion barrier <90 kJ mol^{-1}), the methyl group in the inner 1 position of **5** blocks the inversion of the helix (*vide infra*).‡ (±)-**5** crystallized in the $P2_1/n$ centro-symmetric space group, with heterochiral dimers of *P* and *M* enantiomers, and displays a helicity higher than **3** (50.81°), while the *p*-tolyl group forms a dihedral angle of 43.67° with the imidazolium cycle (Scheme 1, SI). **5** can be regarded as a 1*N*-Me-[5]helicene derivative.[12]

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The heteroleptic cycloiridiated complexes $\mathbf{A}^{1,2}$, bearing a [5]helicene-NHC-*N*-tolyl and two 2-(2,4-difluorophenyl)-pyridyl (dfppy) ligands, were obtained by reacting **5** with Ag_2O and $[Ir(\mu\text{-}Cl)(dfppy)_2]_2$ **6** (Scheme 1, SI).[5,13] The diastereoisomeric mixture of $\mathbf{A}^1$ and $\mathbf{A}^2$ was obtained in the respective 63:37 ratio, as estimated via ^{1}H NMR spectroscopy and HPLC (SI), suggesting that the cyclometalation is diastereoselective. $\mathbf{A}^{1,2}$ correspond to the meridional geometric isomers, indicating that the mutually *trans* disposition of the pyridyl rings of the precursor **6** is retained,[5,13] as further evidenced by ^{1}H-^{1}H NOESY and ^{1}H-^{19}F HOESY NMR studies (SI). X-ray crystallography of the pure diastereoisomer $\mathbf{A}^1$ ($I4_1/a$ centro-symmetric space group, Figure 1, SI) shows the pseudo-octahedral geometry around the iridium center and the *trans* relationship of the pyridyl rings of the two dfppy ligands, whereas the [5]helicene-NHC chelate orientates in two ways around the Ir(III), defining either the Δ_{Ir} or Λ_{Ir} epimers associated respectively with the *M* or *P* helical stereochemistry ((M,Δ_{Ir})- and (P,Λ_{Ir})-$\mathbf{A}^1$) [the other diastereoisomers are (P,Δ_{Ir})- and (M,Λ_{Ir})-$\mathbf{A}^2$]. It depicts also the chiral, purely helical, N-heterocyclic carbenic ligand, with its five *ortho*-fused rings and the NHC cycle bound to the Ir with C2–Ir bond-length of 2.051 Å, and C2–N1 (C2–N3) of 1.368 (1.366) Å.[14] Furthermore, the C2' of the tolyl group is coordinated to the metal (C2'–Ir: 2.102 Å) and is almost coplanar with the NHC cycle (dihedral angle: 3.92°). These metric data correspond to classical values for carbenic cycloiridiated complexes.[5c-e] The ^{13}C NMR spectra of $\mathbf{A}^{1,2}$ show the signal of the carbenic carbon at 187.2 ppm (SI).[5]

Calculations[15] (SI) demonstrate the extended π-conjugation between the NHC unit and the other fused phenyl rings within the π-helical carbenic ligand along with efficient electronic interaction between the [5]helicene-NHC and the metal center. For example, the HOMO (H) and H-2 of $\mathbf{A}^{1,2}$ span over Ir and the helicene-NHC-tolyl, while the LUMO (L) and L+2 correspond almost purely to the helicene-NHC π-helical system (Figure 2c, SI). The strong interaction between the π-helical NHC and Ir(III) has been confirmed with ETS-NOCV charge and bonding energy decomposition analyses (SI),[15b] which revealed a dative NHC-metal bond with NHC→Ir σ-donation and Ir→NHC back-donation, typical for carbenic ligands,[15c] and with the π-back-bonding clearly enhanced due to the extended π-helicene system. These electronic features may account for the good stability and unprecedented photophysical and (chir)optical properties of $\mathbf{A}^{1,2}$ (*vide infra*).

Since the methyl group at the N1 position blocks the helical inversion, enantiomerically enriched samples of (M,Δ_{Ir})- and (P,Λ_{Ir})-$\mathbf{A}^1$ and of (M,Λ_{Ir})- and (P,Δ_{Ir})-$\mathbf{A}^2$ were prepared by HPLC separation over chiral stationary phases (*ee*'s 96-99%, SI).† Refluxing of stereoisomerically pure samples in chloroform for several hours did not lead to any epimerization process, showing the high configurational stability of the [5]helicenic carbene ligand (inversion barrier >125 kJ mol^{-1}) and the Ir center. Electronic circular dichroism (ECD) spectra in CH_2Cl_2 are depicted in Figure 2a. Each pair of enantiomers reveal mirror-image spectra, with (P,Λ_{Ir})-$\mathbf{A}^1$ displaying a set of two positive ECD bands at 252 nm ($\Delta\varepsilon$ = +38 M^{-1} cm^{-1}) and 276 (+43), another set of two positive ECD bands at 312 (+73) and 340 (+58), and a weak negative band at 402 (-14), and (P,Δ_{Ir})-$\mathbf{A}^2$ showing bands at 257 nm ($\Delta\varepsilon$ = +78 M^{-1} cm^{-1}), 278 (-38), 302 (-44), 332 (40), and 403 (-13). Interestingly, (P,Λ_{Ir})-$\mathbf{A}^1$ and (P,Δ_{Ir})-$\mathbf{A}^2$ possess ECD bands at similar wavelengths but some with an opposite sign (e.g. at ca. 275 and 305 nm). Furthermore, the positive intensity around 255 / 335 nm is visibly increased / decreased for (P,Δ_{Ir})-$\mathbf{A}^2$ *vs.* (P,Λ_{Ir})-$\mathbf{A}^1$. All these features reflect the impact of the pseudo-octahedral iridium stereochemistry. Effects of both Ir and helicene-NHC chirality is further demonstrated by a comparison of the ECD spectra for $\mathbf{A}^{1,2}$ and for the model NHC complex **A**.[5c] The sign pattern of bands for Λ_{Ir}-**A** and (P,Λ_{Ir})-$\mathbf{A}^1$ is mostly similar but **A** reveals significantly decreased ECD intensity (not exceeding 30 M^{-1} cm^{-1}), evidently due to the lack of the helicene (Figure 2a). Note also that the calculated ECD spectra for the parent *P*-[5]helicene-NHC species are blue-shifted and less intense compared to (P,Λ_{Ir})-$\mathbf{A}^1$, which confirms the reinforcing impact of the metal and helicene-NHC stereochemistry. See SI for all simulated spectra and molecular orbital analysis. The experimental molar rotations (MRs) also reflect differences between the two epimers (SI). (P,Λ_{Ir})-$\mathbf{A}^1$ displays a strong positive MR at 436 nm (+16520° cm^2 dmol^{-1}) while (P,Δ_{Ir})-$\mathbf{A}^2$ exhibits a negative MR (-2170), suggesting that the contribution of the Δ_{Ir} center compensates and even surpasses the one from the *P*-[5]helicene-NHC.

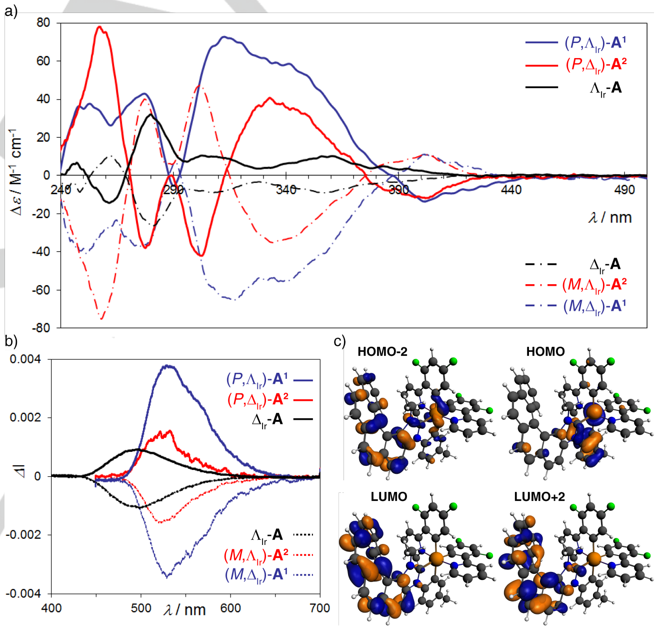

Figure 2. a) ECD spectra of (P,Λ_{Ir})-$\mathbf{A}^1$ and (P,Δ_{Ir})-$\mathbf{A}^2$, of their mirror-images (M,Δ_{Ir})-$\mathbf{A}^1$ and (M,Λ_{Ir})-$\mathbf{A}^2$, and of Λ_{Ir}-/Δ_{Ir}-**A**. b) CPL spectra of (M,Δ_{Ir})-/(P,Λ_{Ir})-$\mathbf{A}^1$, (M,Λ_{Ir})-/(P,Δ_{Ir})-$\mathbf{A}^2$ and Δ_{Ir}-/Λ_{Ir}-**A** at r.t. Each spectrum is normalized to the maximum of its photoluminescence spectrum. c) Isosurfaces (0.04 au) of selected MOs of (P,Λ_{Ir})-$\mathbf{A}^1$.

The efficient interaction between the π-helical NHC and Ir(III) is also reflected in the emission properties of $\mathbf{A}^{1,2}$ (SI). Both complexes display vibrationally structured light-green phosphorescence with the 0,0 band maximum at 525 nm and quantum yields of ca. 9-13%. The $\mathbf{A}^{1,2}$ emission is red-shifted compared to that of the NHC model **A** which displays a blue-green phosphorescence with the 0,0 band at 498 nm. Particularly striking are the phosphorescence lifetimes of ~300 μs observed for $\mathbf{A}^{1,2}$ which are much longer than values of 1 μs typically recorded for tris-cyclometalated Ir(III) complexes, or the 3.1 μs observed for **A**. *The measured lifetimes are amongst the longest reported for cycloiridiated systems.*[16,17] As a result, the luminescence of these complexes is extremely sensitive to oxygen. Lifetimes decrease by a factor of greater than 500 upon aeration of the samples in solution at r. t. (Table S2 in SI). The bimolecular rate constants for quenching by oxygen are of the order of $8.5\cdot10^{8}$ M^{-1} s^{-1} (estimated from the lifetimes under these conditions), which are typical of diffusional quenching for molecular phosphors in solution. Efficient sensitisation of singlet oxygen may be anticipated.[18] Time-dependent DFT (PBE0/SV(P), CH_2Cl_2 continuum solvent model, SI) calculations[15a] correctly reproduce changes in the phosphorescence energies for **A**^{1,2} *vs.* **A** and link the emission features of **A**^{1,2} to the extended π-conjugation in the helical NHC ligand. For **A**, the phosphorescene transition is Ir→dfppy metal-ligand (ML) charge transfer (CT).[5c] In contrast, the T_1 excited state of **A**^{1,2}, exhibiting mixed Ir-NHC-tolyl-helicene,dfppy→NHC-helicene ML / intraligand / ligand-ligand CT character, is strongly delocalized across the [5]helicene-NHC, which lowers its energy. Lesser Ir orbital participation (lesser MLCT character) in the T_1 emission for **A**^{1,2} *vs.* **A** is consistent with the increase in the emission lifetime for the former and indicates that the spin-orbit coupling at the metal ion in **A**^{1,2} is attenuated, yet still sufficient to promote the formally spin-forbidden $T_1 \rightarrow S_0$ process to the extent that it can compete with non-radiative decay.[16] The result is interesting to compare with platinahelicenes, which reveal relatively long-lived phosphorescence in an even more red-shifted region (620 nm) but with shorter lifetimes (20 μs).[19]

Circulary polarized luminescence (CPL) spectra of all enantiopure stereoisomers of **A** and **A**^{1,2} were measured in deoxygenated CH_2Cl_2 samples ($C \sim 10^{-5}$ M) and are depicted in Figure 2b. Each pair of enantiomers display mirror-image CP phosphorescence with dissymmetry factors[20] g_{lum} of $+9\cdot10^{-4}$ at 493 nm for (Δ_{Ir})-**A**, and of $+3.7\cdot10^{-3}$ and $+1.5\cdot10^{-3}$ at 530 nm for respectively $(P,\Lambda_{\mathrm{Ir}})$-**A**^{1} and (P,Δ_{Ir})-**A**^{2}, revealing that the stereochemistry of the π-helical NHC ligand controls the sign of the CPL signal with a value 3 times higher for epimer $(P,\Lambda_{\mathrm{Ir}})$-**A**^{1} *vs.* (P,Δ_{Ir})-**A**^{2}. Here again, manipulating the Ir(III) stereochemistry enables the CPL to be modified.

In summary, this new diversification in organometallic helicene chemistry provides the molecules with unprecedented features and opens a new field, namely NHCs in helicenes. The Ir-NHC-helicene complexes display very long-lived CP blue-green phosphorescence which may lead to future applications as chiral dopants in CP-OLEDs,[21a] singlet oxygen sensitizers, orselective photo-oxidizing agents.[4j,18,21b]

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Keywords: helicenes, chiral N-heterocyclic carbenes, cycloiridiated complexes, chiroptical properties, phosphorescence

Notes and references

‡ Attempts to enantiomerically resolve **5** have failed. Indeed, semi-preparative and analytical separations of helical salts are very rare. See: a) D. Koval, L. Severa, L. Adriaenssens, J. Vavra, F. Teply, V. Kasicka, *Electrophoresis* **2011**, *32*, 2683; b) G. M. Labrador, J. Bosson, Z. S. Breitbach, Y. Lim, E. R. Francotte, R. Sabia, C. Villani, D. W. Armstrong, J. Lacour, *Chirality* **2016**, *28*, 282.

† The diastereomeric mixture of **A**^{1} and **A**^{2} was eluted with hexane / 2-PrOH / chloroform (7/1/2 : v/v/v) on Chiralpak IA to obtain (M,Δ_{Ir})-**A**^{1}, $(M,\Lambda_{\mathrm{Ir}})$-**A**^{2} and the mixture of $(P,\Lambda_{\mathrm{Ir}})$-**A**^{1} and (P,Δ_{Ir})-**A**^{2}, which was subsequently separated on (S,S)-Whelk-O1 column. See SI for details.

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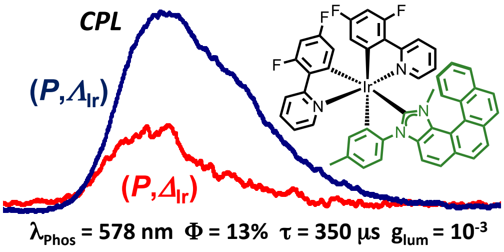
Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

The first fused π-helical N-heterocyclic system has been prepared and examined through its enantiomerically and diastereoisomerically pure cycloiridiated complexes. The systems display long-lived circularly polarized phosphorescence, attributed to the extended π-conjugation within the helical carbenic ligand efficiently interacting with the Ir(III) center.



λ_{Phos} = 578 nm Φ = 13% τ = 350 μs $g_{lum} = 10^{-3}$

N. Hellou, M. Srebro-Hooper, L. Favereau, F. Zinna, E. Caytan, L. Toupet, V. Dorcet, M. Jean, N. Vanthuyne, J. A. G. Williams, L. Di Bari, J. Autschbach, and J. Crassous**

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Enantiopure cycloiridiated complexes bearing a pentahelicenic N-heterocyclic carbene and displaying long-lived circularly-polarized phosphorescence