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To be cited as: *Helv. Chim. Acta* 10.1002/hlca.201900044

Link to VoR: http://dx.doi.org/10.1002/hlca.201900044

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10.1002/hlca.201900044

An enantiopure cyclometallated iridium complex displaying long-lived phosphorescence both in solution and in the solid state

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This article is dedicated to François Diederich on the occasion of his retirement.

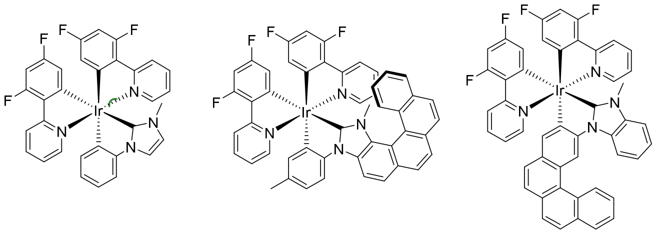
A new enantiopure cyclometallated iridium complex bearing a [4]helicenic :C^C^{-} and two :N^C^{-} dfppy (2-(2,4-difluorophenyl)-pyridyl) ligands was prepared. This complex revealed a long-lived phosphorescence both in solution and in the solid state. Its chiroptical properties, namely electronic circular dichroism and circularly polarized luminescence, were also examined. Comparison with former chiral complexes enabled assignment of the Δ_{Ir}-(-) and Λ_{Ir}-(+) absolute configurations.

Keywords: iridium • cyclometallated • helicene • optical activity • long-lived phosphorescence

Introduction

Cyclometallated iridium(III) complexes[1-3] attract ever-increasing attention in the field of phosphorescent materials. They are being investigated for high-efficiency organic light-emitting devices (OLEDs),[4,5] as intracellular luminescence probes, as anticancer or antibacterial agents,[6,7] and in photocatalysis.[8] Few examples of enantiopure cyclometallated Ir(III) complexes have been reported to date.[3,9-17] *N*-heterocyclic carbenes (NHCs) are good ligands for conceiving chiral organometallic complexes,[18,19] including cycloiridiated complexes. Since NHCs are strong-field ligands, NHC-based cycloiridiated complexes may display interest as deep blue phosphors, a particularly challenging target in the OLED area.[20-27] Moreover, if a single enantiomer of such chiral complexes can be isolated, then the possibility of exploiting chiroptical properties such as its circular polarisation is opened up. In this context, we have recently shown for the first time that helicene-based NHCs can be synthezised, giving access to enantiopure iridium complexes that display strong chiroptical properties, especially intense electronic circular dichroism (ECD)[28] and long-lived circularly polarized phosphorescence (CPL).[29,30-31] More specifically, we have described the first synthesis of a diastereomerically pure π-conjugated *ortho*-fused [5]helicenic complex **B**,[29] having a cycloiridiated core with meridional geometry, as in the corresponding non-helicenic model complex **A**[22](Figure 1).

In compound **B,** the NHC unit was incorporated within a helical core. In this contribution, we describe a new helicenic complex **C**, related to **B**, but in which the carbene ligand bears a [4]helicenic fragment attached to one nitrogen atom of the benzimidazole-based NHC unit, therefore not fully fused with the NHC. We detail its synthesis in racemic and enantiopure forms, together with its photophysical (UV-vis absorption and emission) and chiroptical (optical rotation and electronic circular dichroism, circularly polarized luminescence) properties.



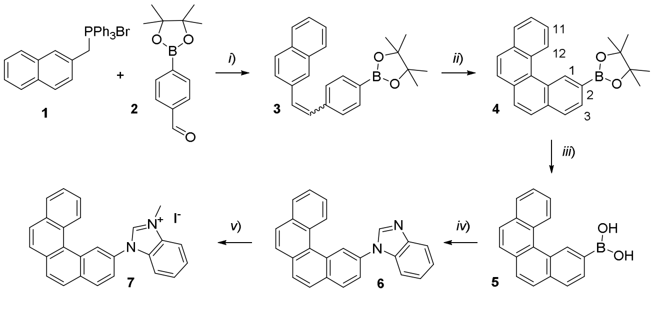
***mer*-Δ_{Ir}-A** ***mer*-(Δ_{Ir},*P*)-B** ***mer*-Δ_{Ir}-C**

Figure 1. Chiral cycliridiated complexes: small model complex **A** (with a meridional arrangement of the formally anionic, metallated carbon atoms);[22] the related complex **B** bearing a [5]helicenic NHC ligand;[29] and the new complex **C** described in this work.

Results and Discussion

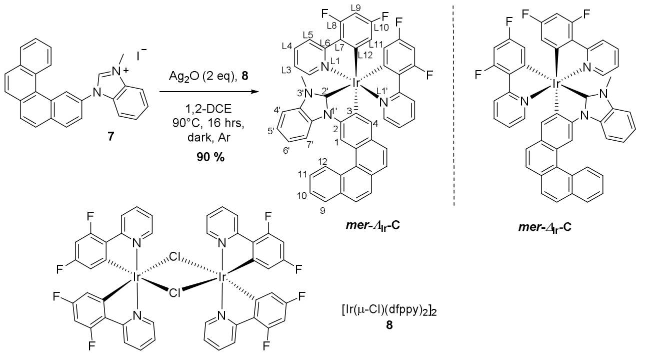
Synthesis of cycloiridiated complex C bearing a [4]helicenic NHC ligand.

In targeting complex **C**, a route to the [4]helicene-2-benzimidazolium salt **7** was first devised, as shown in Scheme 1. We recently reported that helicene boronate derivatives can be obtained via oxidative photocylization, a classical method for preparing helicenic derivatives,[32] and that these boronates can subsequently be used as key intermediates to access carbohelicenes substituted with diverse *N*-containing functionalities.[33] Using such an approach, we synthesized a [4]helicene-boronate system as a key precursor for further functionalization with an imidazole via a Chan-Lam coupling. Firstly, [4]helicen-2-pinacolboronate **4** was synthesized in 56% yield in two steps: a classical Wittig reaction between (naphthalen-2-ylmethyl)triphenylphosphonium bromide **1** and 4-formylphenyl boronic acid pinacol ester **2** to give **3** as a 91/9 *Z*/*E* isomeric mixture, followed by an oxidative photocyclization in the presence of stoichiometric iodine and an excess of propylene oxide.[34] The ^{1}H NMR spectrum of **4** shows the typical deshielded signals found in [4]helicenic structures: a singlet at 9.63 ppm for H^1 and a doublet at 9.21 ppm for H^{12} (see numbering on Scheme 2). The pinacolate was removed by treatment with sodium periodate and ammonium acetate in an acetone/water solvent mixture,[35] giving the [4]helicenic boronic acid **5** in 98 % yield. The preparation of [4]helicene-2-benzimidazolium iodide **7** was then achieved in two steps. First, a Chan-Lam[36,37] coupling between the boronic acid **5** and benzimidazole, using Cu_2O as the copper source in methanol open to the air,[38] yielded [4]helicene-2-benzimidazole **6** in 63% yield. This compound was then *N*-methylated by treatment with an excess of methyl iodide, to give the imidazolium salt **7** in 85% yield. The structure of the benzimidazolium salt **7** was confirmed by ^{1}H NMR spectroscopy, which revealed the presence of a singlet at 9.36 ppm and a doublet at 9.13 ppm, corresponding to protons H^1 and H^{12} respectively. Furthermore, the singlet at 9.63 ppm is typical of proton H$^{2'}$,[22,29] while the singlet at 4.24 ppm corresponds to the *N*-methyl substituent.



Scheme 1. Synthesis of imidazolium salt **7**. Reagents: *i)* *n*-BuLi, THF, rt, 16 h, 75%; *ii)* hν, I_2 (1 equiv.), propylene oxide (40 equiv.), toluene, 8 h, 74%; *iii)* $NaIO_4$, NH_4OAc, acetone/H_2O, rt, 7 d, 98%; *iv)* benzimidazole, Cu_2O, MeOH, 60°C, 16 h; 63%, v) CH_3I, large excess, rt, 16 h, 85%.

Having in hand the [4]helicene-2-benzimidazolium salt **7**, we then investigated the preparation of the cyclometallated iridium(III) complex **C** bearing a [4]helicene-NHC bidentate ligand. The synthesis was performed according to a known procedure, namely the *in situ* deprotonation of **7** in the presence of Ag_2O, giving an intermediate silver(I) complex, which was transmetallated by reaction with *trans*-[Ir(dfppy)$_2$(μ-Cl)]$_2$ **8** {dfppy = 2-(2,4-difluorophenyl)-pyridyl} in the conditions depicted on Scheme 2.[22,29] The heteroleptic cycloiridiated complex **C** was obtained in 90 % yield after purification by chromatography on silica.



Scheme 2. Synthesis of the meridional cycloiridiated complex **C** from [Ir(dfppy)$_2$(μ-Cl)]$_2$ (**8**) and benzimidazolium salt **7**.

The ^{1}H NMR spectrum (see Supplementary Information, SI) shows the presence of a singlet at 9.70 ppm and a doublet at 9.43 ppm, corresponding to H^1 and H^{12} respectively of the helicenic unit, and the typical signals between 5.8 and 6.7 ppm for protons H^{L9}, H$^{L9'}$ and H^{L11}, H$^{L11'}$ which are coupled to fluorine atoms. The ^{13}C NMR spectrum displays a signal at 188.8 ppm corresponding to the carbenic carbon atom.[22,29] The structure of complex **C** was confirmed by X-ray crystallography.# The X-ray structure of racemic **C** (*P-1* centro-symmetric space group, Figure 2 and SI) shows a pseudo-octahedral geometry around the iridium center and a meridional (*mer*) arrangement of the metallated (formally anionic) carbon atoms. The pyridyl rings of the dfppy ligands are orientated *trans* to one another, as in the precursor **8**. The [4]helicene-NHC chelate orientates in two ways around the Ir(III) to define either the Δ_{Ir} or Λ_{Ir} enantiomers. The carbenic NHC ligand displays a C$^{2'}$–Ir bond length of 2.104 Å, and C$^{2'}$–N$^{1'}$ and C$^{2'}$–N$^{3'}$ bond lengths of 1.380 and 1.351 Å, respectively. The C^3 carbon of the [4]helicenic moiety is coordinated to the Ir center (C^3–Ir bond length: 2.059 Å) and the C-Ir-C plane is almost coplanar with the phenyl ring of the helicene (dihedral angle of 2.80°). These metric data are similar to corresponding values for other reported carbenic cycloiridiated complexes.[20-31] The [4]helicenic part displays a helicity (dihedral angle between terminal rings) of 29.07° in the solid state, but it is not configurationally stable in solution (only one pair of enantiomers, *vide infra*). It may be noted that upon coordination to iridium, the π-system has been further elongated to seven fused aromatic rings, including the carbenic ring. However, as these rings are not all in *ortho*-fused positions, the ligand remains a [4]helicenic system. Overall, these features have a direct impact on the photophysical properties of the molecule.

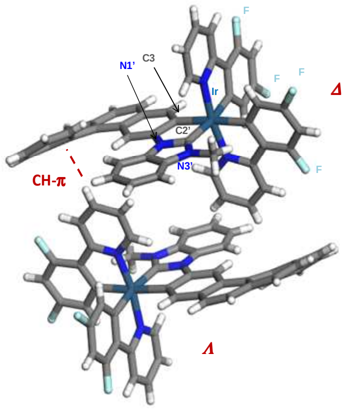


Figure 2. X-ray structure complex of *mer*-C (unit cell containing the two Δ_{Ir} / Λ_{Ir} enantiomers).

Photophysical properties of the iridium(III) complex C

Bis- and tris-cyclometallated iridium(III) complexes are often highly luminescent in solution, emitting from triplet states. The archetypal systems *fac*-Ir(ppy)$_3$ and *cis*-[Ir(ppy)$_2$(bpy)]$^+$ have been complemented over the past two decades by a large array of derivatives, including systems that feature carbenic :C^C$^-$-coordinating ligands in place of one or more of the :N^C$^-$ ligands.[4,5,20-24] The replacement of the heterocyclic ligating unit by a carbene typically attenuates the π acceptor nature, leading to destabilisation of metal-to-ligand charge-transfer excited states and hence to blue shifted absorption and emission.

The absorption and emission properties of the racemic complex **C** were studied in dichloromethane solution at room temperature; emission was also examined in a frozen glass at 77 K and in the solid state at room temperature. Spectra are displayed in Figures 3 and pertinent data are collated in Table 1. The absorption spectrum displays the expected very intense absorption in the far-UV region associated with π-π* transitions of the ligands, together with bands in the near-UV extending beyond 400 nm into the visible region. The spectrum is indeed quite similar to that of *fac*-Ir(ppy)$_3$; there is no significant red-shift, despite the presence of the highly conjugated helicene. In deoxygenated CH_2Cl_2 at room temperature, the complex displays a vibrationally structured phosphorescence spectrum, with well-defined emission maxima at 510, 549, 690 and 660 nm, a modest quantum yield of 5%, and a very long luminescence lifetime of 140 µs. The emission of **C** is bathochromically shifted compared to that displayed by the non-helicenic Ir(III) carbene complex **A** (Figure 1), which has λ_{max} = 483 nm under the same conditions.[22] Moreover, the spectral profile of that complex is very different – a broad band with essentially no discernible vibrational structure. These differences may be attributed to the presence of the extended π-conjugated system of the helicene, which allows delocalization of the electron density over the helix. Indeed, the highly structured character of the emission bands suggests an excited state that is much more heavily localized on the π-system, albeit with some contribution from ^{3}MLCT-type transitions. Such a difference in the nature of the excited state also accounts for the much longer luminescence lifetime of 140 µs for **C** compared to 1.8 µs for **A**, the formally forbidden $T_1 \rightarrow S_0$ phosphorescence process being promoted less efficiently as the MLCT character decreases. Somewhat similar observations were made for our previously investigated complex **B** (Figure 1).[29]

In a frozen glass at 77 K, the emission profile is only slightly displaced to shorter wavelengths (Figure 3, left), which suggests that, even at room temperature, there is little distortion in the triplet excited state relative to the ground state, probably reflecting the rigid nature of the helicene system. The lifetime under these conditions increases to around 1 ms, and indeed the temporal decay of the green emission is easily visible to the naked eye.

The emission from solution at room temperature is very efficiently quenched by oxygen: in air-equilibrated CH_2Cl_2, the luminescence is very weak indeed, such that an accurate lifetime under these conditions could not be determined. Given the efficacy of oxygen quenching, efficient production of the $^1\Delta_g$ state of O_2 – "singlet oxygen" – might be anticipated. Indeed, a band centred at 1274 nm, corresponding to the $^1\Delta_g \rightarrow {}^3\Sigma_u$ transition of oxygen, was readily observed when the emission spectrum of the sample was recorded using a near-infrared detector. The quantum yield of singlet oxygen production was estimated to be 0.6 ± 0.1 using phenalenone as a standard, for which $\Phi(^1\Delta_g)$ = 0.98 under the same conditions. This result is in line with a recent study that reported singlet oxygen generation by lanthanide complexes bearing a helicene-bipyridine ligand.[39]

The emission of most cyclometallated iridium(III) complexes tends to be severely quenched in the solid state, with large reductions in the photoluminescence quantum yields compared to values in solution. Such effects, attributed to triplet-triplet annihilation (TTA) and associated processes, also mean that the internal electroluminescence efficiencies (EQE) of doped OLED devices drop off sharply with increased loadings within the emitting layer. We were curious to investigate the photoluminescence properties of complex **C** in the solid state, given the different nature of its emissive excited state localized on the helicene, compared to more conventional systems. Remarkably, **C** remains highly luminescent in the solid state, with a strongly red-shifted emission around 615 nm and the emission profile remains extraordinarily well structured (Figure 3, right, vibronic progression of ~1360 *vs.* 1420 cm^{-1} in solution at rt). Indeed, the luminescence lifetime of 960 µs recorded under these conditions is only marginally less than that in a dilute rigid glass at 77 K. Apparently, therefore, non-radiative decay processes are unusually well suppressed in the solid. Whilst it might be appealing to attribute both these unusual observations to the relative isolation of the helicene in the structure, it is interesting to note that the emission maxima are red-shifted compared to the values in solution, perhaps suggesting the involvement of dimeric or aggregate excited states that extend over two or more molecules in the solid state.[40] A closer look at the crystal structure revealed the presence of CH-π interactions between H^{L4}- and the terminal ring of the [4]helicene unit (see Figure 2, H^{L4}-centroid interaction distance 3.020 Å) but no clear π–π interaction, although the compound does appear closely packed. Notwithstanding the lack of a fully convincing explanation, the empirical observation of intense, long-lived, and vibrationally structured photoluminescence in the solid state renders complex **C** particularly intriguing amongst the many cyclometallated Ir(III) phosphors reported to date.

Table 1. Absorption and photoluminescence data of complex **C** (in CH_2Cl_2 at 298 K, except where indicated otherwise).

Absorption λ_{max} / nm (ε /$M^{-1}cm^{-1}$)	**Emission λ_{max} / nm**	**Φ_{lum}** [a]	**τ_{lum} / µs** [a]	**Emission λ_{max} / nm (77 K)** [b]	**τ_{lum} / µs (77 K)** [b]
394 (8600), 374 (12900), 307 (69500), 250 (96500)	510, 549, 690, 660	0.05	140	503, 542, 589, 635	1030

[a] In deoxygenated solution. [b] In diethyl ether / isopentane / ethanol (2:2:1 v/v).

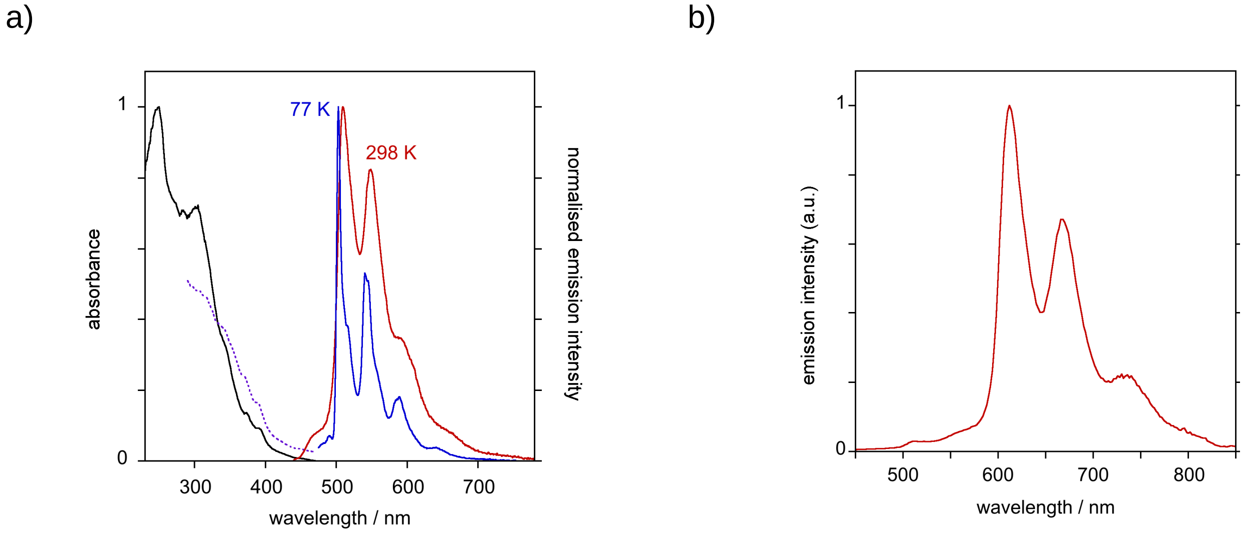


Figure 3. Left: a) Absorption (black line), emission (red line, λ_{ex} = 430 nm) and excitation (dashed purple line, λ_{em} = 547 nm) spectra of complex **C** in CH_2Cl_2 at 298 K; and the emission spectrum at 77K (blue line) in diethyl ether / isopentane / ethanol (2:2:1 v/v). b) Emission spectrum of complex **C** in the solid state at 298 K, λ_{ex} = 430 nm.

Chiroptical properties of enantiopure complex C

Thanks to its neutral character, good chemical stability and good solubility in organic solvents, [4]-helicenic-NHC-based cycloiridiated complex **C** was readily resolved into enantiomers by HPLC over a chiral stationary phase (Chiralpak IG, using hexane/ethanol/dichloromethane (70/5/25) as the mobile phase, see SI). Enantiomeric excesses higher than 98.5% were achieved in this way. The enantiomers displayed specific optical rotations values of +510 and -517 in CH_2Cl_2 at 6-10 × 10^{-4} M concentrations. The electronic circular dichroism spectra of both enantiomers were also measured under the same conditions and are depicted in Figure 4. They display mirror-image relationship, with bands of moderate intensities at 232 nm ($\Delta\varepsilon$ = +25 M^{-1} cm^{-1}), 250 and 255 nm ($\Delta\varepsilon$ = -69 and -62 M^{-1} cm^{-1}), 282 nm ($\Delta\varepsilon$ = +16 M^{-1} cm^{-1}), 305 and 330 nm ($\Delta\varepsilon$ = -31 and -35 M^{-1} cm^{-1}), 364 and 388 nm ($\Delta\varepsilon$ = -11 and -8 M^{-1} cm^{-1}). Comparison of specific rotation values and of ECD spectra with the model system **A** enables assignment of the $\mathit{\Delta}_{Ir}$-(-) and $\mathit{\Lambda}_{Ir}$-(+) absolute configurations for complex **C**. Some similarities with the ECD signature of complex (P,$\mathit{\Lambda}_{Ir}$)-**B** was also noticed, such as the two strong bands at 250 nm and between 300-330 nm (see Figure S15 in SI) suggesting that the [4]helicenic part fused with the iridacycle has a similar effect on the ECD activity as the fused [5]helicenic-NHC-iridacycle core.

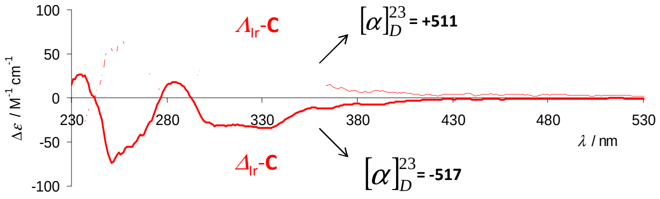


Figure 4. ECD spectra of complex $\mathit{\Delta}_{Ir}$-(-) and $\mathit{\Lambda}_{Ir}$-(+)-**C** in dichloromethane.

Finally, the circularly polarized luminescence (CPL) of this new enantiopure chiral emissive cycloiridiated complex was studied.[41-43] The CPL responses for $\mathit{\Delta}_{Ir}$-(-) and $\mathit{\Lambda}_{Ir}$-(+)-**C** were measured in CH_2Cl_2 at rt and the resulting spectra are depicted in Figure 5, showing maximum g_{lum} = $2\Delta I/I$ values of -2.6 and +3.1 × 10^{-3} for $\mathit{\Lambda}_{Ir}$-(+)-**C** and $\mathit{\Delta}_{Ir}$-(-) at ~513 nm, respectively. These values appear quite similar to those of model complexes **A** and **B** (absolute values between 2 and 4 × 10^{-3})[29] and enable to confirm again the absolute configuration at

Ir center from model **A**. Note however that CPL in the solid could not be measured, despite several attempts.

Conclusions

In conclusion, a novel cycloiridiated complex bearing a helicenic NHC ligand has been prepared in enantiopure forms. The synthesis relied on the preparation of a [4]helicenic boronic acid which was coupled to a benzimidazole unit. After *N*-methylation and reaction with an iridium precursor, complex **C** was obtained in racemic form and was subsequently resolved into its enantiomers by chiral HPLC. Its photophysics and chiroptical activity was studied and compared to model complexes **A** and **B** without and with a helical structure, respectively. Interestingly, long-lived green phosphorescence and singlet oxygen generation were observed in dichloromethane solutions at room temperature while a long-lived red phosphorescence was observed in the solid state. Finally, complex **C** displayed similar CPL activity as analogues **A** and **B**. These features make the family of cycloiridiated complexes decorated with a helicenic ligand interesting chiral phosphors with potential applications in chiral molecular materials, biological imaging, enantioselective catalysis or photodynamic therapy.

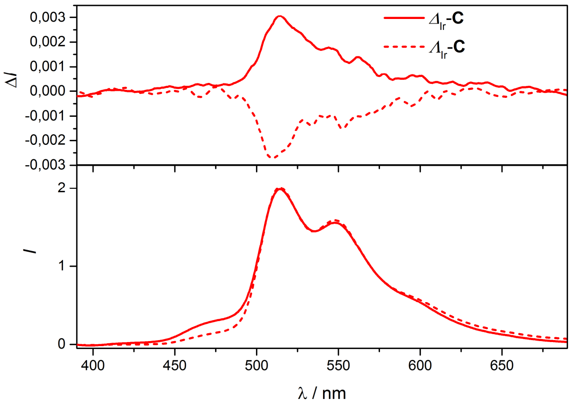


Figure 5. Emission and CPL spectra of Δ_{Ir}-(-)-**C** (solid red) and Λ_{Ir}-(+)-**C** (dashed red) in carefully deaerated CH_2Cl_2 solutions at rt (C ~ 1.10^{-5} M). Excitation wavelength λ_{ex} at 350nm.

Experimental Section

General Experimental Information

Solvents were freshly distilled under argon from sodium / benzophenone (THF) or from calcium hydride (MeOH). All commercially available chemicals were used without further purification. Column chromatography purifications were performed over silica gel (Acros, 0.063–0.200 mm). Irradiation reactions were conducted using a Heraeus TQ 700 mercury vapor lamp. NMR spectra were recorded at room temperature on a Bruker AV III 400 MHz equipped with a tunable BBFO probe, and a Bruker Av I 500 MHz fitted with a TCI cryoprobe (Biosit platform, Université de Rennes 1). ^{1}H, ^{13}C and ^{19}F chemical shifts are reported in parts per million (ppm) relative to Me$_4$Si as external standard. Assignment of proton, carbon and fluorine signals is based on COSY, band-selective HSQC and HMBC, and ^{1}H-^{19}F hetero-COSY experiments. ^{1}H-^{1}H and ^{1}H-^{19}F dipolar couplings were studied using NOESY or HOESY sequence, with a 500 ms or 800 ms mixing time,respectively. Mass spectrometry was performed by the CRMPO, University of Rennes 1, on a Thermo Fisher Q-Exactive or Brucker MaXis 4G using ESI technique. Melting points were measured on a melting point apparatus Stuart SMP10. Specific rotations (in deg cm^{3}g^{-1}) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in M^{-1}cm^{-1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility (Biosit platform, Université de Rennes 1). UV/vis spectroscopy was conducted on a Varian Cary 5000 spectrometer. Chiral high-performance liquid chromatography (HPLC) was performed by iSm2, Aix Marseille University, on an Agilent Technologies 1260 Infinity with Igloo-Cil ovens, using Jasco OR-1590 and CD-2095 as polarimetric and circular dichroïsm detectors. The conditions for HPLC separations are described in the SI part.

Synthesis

4’,4’,5’,5’-Tetramethyl-2’-(4-(2-(naphthalen-2-yl)vinyl)phenyl)-1’,3’,2’-dioxaborolane 3. (Naphthalen-2-ylmethyl)triphenylphosphonium bromide **1** (1.8 g, 3,73 mmol) was suspended in 75 mL of anhydrous THF under argon and cooled to -78 °C. To the suspension, was added dropwise *n*-BuLi (2.5 M in hexanes, 1.5 ml, 3.75 mmol). The resulting solution was stirred at -78 °C for 10 min, then warmed to room temperature and stirred for 30 min. The solution was cooled again to -78 °C, and (4-formylphenyl)boronic acid pinacol ester **2** (832 mg, 3.58 mmol) in anhydrous THF (2 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 16 hours. Pentane was added and the mixture was filtered on Celite. Evaporation of the solvent and purification of the oily residue by column chromatography (silica gel, cyclohexane / CH$_2$Cl$_2$, 6/4) afforded **3** as a *Z/E* mixture (91/9) (1.0 g, 75 %) as a yellow solid. Rf = 0.35 and 0.45 (cyclohexane/CH$_2$Cl$_2$: 6/4). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.80 – 7.72 (m, 3H), 7.66 (t, *J* = 8.4 Hz, 3H), 7.45 – 7.43 (m, 2H), 7.36 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.33 (s, 1H), 7.30 (s, 1H), 6.81 (d, *J* = 12.2 Hz, 1H) 6.70 (d, *J* = 12.3 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 140.3, 134.9, 134.8, 133.6, 132.8, 131.0, 130.7, 128.4, 128.2, 128.1, 127.7, 127.6, 127.0, 126.1, 126.1, 83.9, 25.0. ^{11}B NMR (96 MHz, CDCl$_3$) δ 30.9. HRMS (ESI) calculated for [M+Na]$^+$ (C$_{24}$ H$_{25}$ O$_2$ ^{11}B Na): 379.18398, found: 379.1844.

2-(Benzo[*c*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 4. Compound **3** (500 mg, 1.40 mmol) as 91/9 *Z/E* mixture, iodine (355 mg, 1.40 mmol, 1 eq.) and propylene oxide (3.9 mL, 40 eq.) were dissolved in toluene (2.5 L) previously degassed by bubbling argon for 15 mn. The mixture was irradiated for 8 hours using a Heraeus TQ 700 mercury vapor lamp**.** After evaporation of the solvent, a purification by chromatography (silica gel, cyclohexane / CH$_2$Cl$_2$, 7/3) afforded the desired product **4** (368 mg, 74 %) as a yellow solid. Rf = 0.50 (cyclohexane/CH$_2$Cl$_2$: 5/5). Mp = 160-162°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.63 (s, 1H), 9.21 (d, *J* = 8.4 Hz, 1H), 8.06 – 8.00 (m, 3H), 7.93 – 7.81 (m, 4H), 7.76 (ddd, , *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.66 (ddd, *J* = 7.9, 6.8, 1.2 Hz, 1H), 1.41 (s, 12H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 135.8, 135.4, 133.7, 131.1, 131.0, 130.5, 129.8, 128.6, 128.5, 128.1, 128.0, 127.8, 127.6, 127.4, 126.9, 126.5, 126.0, 84.1 (2 C), 25.1 (4 C). ^{11}B NMR (96 MHz, CDCl$_3$) δ 31.5. HRMS (ESI) calculated for [M+Na]$^+$ (C$_{24}$ H$_{23}$ O$_2$ ^{11}B Na): 377.16833, found: 377.1687.

Benzo[c]phenanthren-2-ylboronic acid 5. To a solution of boronate **4** (328 mg, 1.07 mmol) in acetone (70 mL), were added NaIO$_4$ (1.60 g, 7.48 mmol, 7 eq.), NH$_4$OAc (560 mg, 7.27 mmol, 6.8 eq.) and water (35 mL). The resulting mixture was allowed to stir vigorously for 7 days. After evaporation of acetone, the reaction mixture was diluted with ethyl acetate and water. The organic layer was separated, dried over MgSO$_4$ and concentrated under reduced pressure to give benzo[c]phenanthren-2-ylboronic acid **5** as a yellow solid (285 mg, 98 %). The product was directly engaged in the next step without further purification. ^{1}H NMR (300 MHz, DMSO) δ 9.53 (s, 1H), 9.12 (d, *J* = 8.4 Hz, 1H), 8.30 (s, 2H), 8.14 (dd, *J* = 7.5 Hz, 1.5Hz, 1H), 8.10 – 7.93 (m, 6H), 7.77 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H), 7.24 (ddd, *J* = 8.4, 7.8, 1.1 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ 134.3, 133.9, 133.2, 131.1, 130.7, 129.6, 128.9, 128.7, 127.7, 127.5, 127.4, 126.9, 126.8, 126.7, 126.2. HRMS (ESI) calculated for [M+Cl]$^-$ (C$_{18}$ H$_{13}$ O$_2$ ^{35}Cl ^{11}B): 307.07026, found: 307.0706.

1-(Benzo[c]phenanthren-2-yl)-1*H*-benzo[d]imidazole 6. Cu$_2$O (24 mg, 0.17 mmol, 0.2 eq.) was added to a mixture of benzimidazole (120 mg, 1.01 mmol, 1.2 eq.) and benzo[c]phenanthren-2-ylboronic acid **5** (230 mg, 0.85 mmol) in MeOH (5 mL) at room temperature, and the mixture was stirred at 60 °C for 16 hours under an atmosphere of air. The reaction mixture was concentrated under reduced pressure to give product residue which was purified by column chromatography (silica gel, cyclohexane / ethyl acetate 7/3) to afford the [4]helicene-benzimidazole product **6** (185 mg, 63 %) as a beige solid. Rf = 0.10, cyclohexane / AcOEt, 7/3. Mp = 181-183°C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 9.25 (s, 1H), 9.06 (d, *J* = 8.2 Hz, 1H), 8.30 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.05 (dd, *J* = 7.2, 5.3 Hz, 1H), 8.01 – 7.86 (m, 4H), 7.79 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.73 – 7.61 (m, 3H), 7.40 (dt, *J* = 6.1, 3.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.2, 133.6, 132.8, 131.8, 131.0, 130.6, 130.1, 128.9, 128.5, 128.0, 127.2, 127.1, 127.0, 126.9, 126.8, 126.4, 124.0, 123.1, 123.0, 122.0, 120.9, 110.6. HRMS (ESI) calculated for $[M+H]^+$ (C_{25} H_{17} N_2): 345.13862, found: 345.1388.

1-(Benzo[c]phenanthren-2-yl)-3-methyl-1*H*-benzo[d]imidazolium iodide 7. In a dried Schlenk tube was introduced compound **6** (110 mg, 0.32 mmol) in MeI (5 mL) and the mixture was stirred overnight at room temperature. The solvent was evaporated under vacuum (*Caution:* methyl iodide is a carcinogen and must be handled with extreme care). The resulting solid was washed with AcOEt, leading to the desired salt **7** as a white solid (133 mg, 85 %). Mp = 258-260°C (dec). ^{1}H NMR (300 MHz, CD_3CN) δ 9.63 (s, 1H), 9.36 (d, *J* = 2.1 Hz, 1H), 9.13 (d, *J* = 8.9 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 1H), 8.20 – 8.06 (m, 4H), 8.03 – 7.97 (m, 2H), 7.94 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.87 – 7.67 (m, 5H), 4.24 (s, 3H). ^{13}C NMR (75 MHz, CD_3CN) δ 143.0, 135.1, 134.6, 133.2, 133.1, 132.9, 132.1, 131.4, 130.5, 130.2, 129.8, 128.8, 128.4, 128.3, 128.2, 127.74, 127.70, 125.8, 123.3, 114.6, 34.6. HRMS (ESI) calculated for C^+ (C_{26} H_{19} N_2): 359.15427, found: 359.1546 and for $[2C^+,I^-]^+$ (C_{52} H_{38} N_4 I): 845.21357, found: 845.2143.

Cyclometallated iridium(III) complex C.

Imidazolium iodide salt **7** (10 mg, 0.021 mmol), Ag_2O (10 mg, 0.042 mmol), and *trans*-[Ir(dfppy)$_2$Cl]$_2$ **8** (13 mg, 0.011 mmol) were dissolved in 2 mL of 1,2-dichloroethane, and the reaction was heated to 90°C in the dark. After 16h, the solution was allowed to cool to room temperature and filtered through Celite® with CH_2Cl_2 as eluent. Removal of the solvent under reduced pressure afforded the crude product as a yellow solid. Purification by column chromatography over silica gel (95:5 Heptane/AcOEt) afforded the desired yellow complex **1** (18 mg; 90 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.70 (s, 1H, H^{1}), 9.43 (d, *J* = 8.5 Hz, 1H, H^{12}), 8.51 (d, *J* = 8.3 Hz, 1H, H$^{7'}$), 8.27 (t, *J* = 7.9 Hz, 2H, H$^{L5'}$, H^{L5}), 8.15 (d, *J* = 6.0 Hz, 1H, H^{L2}), 8.07 (d, *J* = 8.0 Hz, 1H, H^{9}), 8.03 (d, *J* = 6.0 Hz, 1H, H$^{L2'}$), 7.85 (d, *J* = 8.5 Hz, 1H, H^{8}), 7.81 (d, *J* = 8.0 Hz, 1H, H^{7}), 7.79 (ddd, *J* = 8.4, 6.9, 1.9 Hz, 1H, H^{11}), 7.68 (t, *J* = 7.4 Hz, 1H, H^{10}), 7.65 (d, *J* = 8.5 Hz, 1H, H^{6}), 7.60 (dd, *J* = 7.9, 4.6 Hz, 3H, H^{5}, H$^{L4'}$, H^{L4}), 7.54 – 7.50 (m, 1H, H$^{6'}$), 7.47 – 7.44 (m, 1H, H$^{4'}$), 7.44 (s, 1H, H$^{5'}$), 7.40 (s, 1H, H^{4}), 6.76 – 6.71 (m, 1H, H$^{L3'}$), 6.71 – 6.68 (m, 1H, H^{L3}), 6.54 (ddd, $J_{H\text{-}F}$ = 12.1, 9.5, $J_{H\text{-}H}$ = 2.4 Hz, 1H, H$^{L9'}$), 6.48 (ddd, $J_{H\text{-}F}$ = 11.9, 9.4, $J_{H\text{-}H}$ = 2.3 Hz, 1H, H^{L9}), 6.22 (dd, $J_{H\text{-}F}$ = 7.7, $J_{H\text{-}H}$ = 2.3 Hz, 1H, H^{L11}), 5.86 (dd, $J_{H\text{-}F}$ = 8.3, $J_{H\text{-}H}$ = 2.3 Hz, 1H, H$^{L11'}$), 3.50 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 188.8 ($C^{2'}$), 179.0 (C^{L7}), 177.4 ($C^{L7'}$), 166.8 (C^{L6}), 165.6 ($C^{L6'}$), 154.6 (C^{3}), 153.6 (CH^{L2}), 153.2 ($CH^{L2'}$), 151.1 (C^{2}), 137.8 (CH^{4}), 137.4 ($C^{3a'}$), 136.7 (CH^{L4}), 136.2 ($CH^{L4'}$), 134.0 (C^{8a}), 133.2 ($C^{7a'}$), 132.8 (C^{4a}), 130.8 (C^{12a}), 130.5 (C^{6a}), 129.3 (CH^{9}), 128.4 (C^{L12}), 128.1 (C^{12b}), 127.8 (CH^{12}), 127.75 (CH^{11}), 127.6 ($C^{L12'}$), 127.6 (CH^{5}), 127.5 (C^{12c}), 126.5 (CH^{8}), 126.2 (CH^{7}), 126.15 (CH^{10}), 125.5 (CH^{6}), 124.6 ($CH^{6'}$), 123.7 (d, *J* = 20.8 Hz, $CH^{L5'}$), 123.6 ($CH^{5'}$), 123.4 (d, *J* = 20.7 Hz, CH^{L5}), 123.1 ($CH^{L3'}$), 122.8 (CH^{L3}), 114.3 (dd, *J* = 13.8, 2.7 Hz, CH^{L11}), 112.3 ($CH^{7'}$), 112.2 (dd, *J* = 15.2, 2.2 Hz, $CH^{L11'}$), 111.3 ($CH^{4'}$), 110.3 (CH^{1}), 96.9 (t, *J* = 27.3 Hz, CH^{L9}), 96.9 (t, *J* = 27.1 Hz, $CH^{L9'}$), 34.3 (CH_3). The carbons α to fluorines were not found. ^{19}F NMR (376 MHz, CD_2Cl_2) δ -109.83 (q, *J* = 9.2 Hz, F$^{L10'}$), -110.29 (q, *J* = 9.4 Hz, F^{L10}), -110.42 (t, *J* = 11.3 Hz, F^{L8}), -111.15 (t, *J* = 12.6 Hz, F$^{L8'}$). HRMS (ESI) calculated for $[M+Na]^+$ (C_{48} H_{29} N_4 F_4 Na ^{193}Ir): 953.185, found: 953.1849.

Optical spectroscopy

Absorption spectra were measured in solution in CH_2Cl_2 at room temperature in 1 cm pathlength quartz cuvettes using a Biotek Instruments XS spectrometer. Emission end excitation spectra were recorded using a Jobin Yvon Fluoromax-2 spectrometer equipped with a Hamamatsu R928 photomultiplier tube. For the measurements at 298 K, the solutions were contained within 1 cm pathlength quartz cuvettes modified for connection to a vacuum line. Degassing was achieved by three freeze-pump-thaw cycles whilst connected to the vacuum manifold; final vapour pressure at 77 K was $< 5 \times 10^{-2}$ mbar. The luminescence quantum yield was determined using aqueous [Ru(bpy)$_3$]Cl$_2$ as the standard (Φ = 0.028 in air-equilibrated aqeuous solution).[44] The emission spectrum at 77 K was recorded in a glass of EPA (= diethyl ether / isopentane / ethanol, 2:2:1 v/v) in a 4 mm diameter quartz tube held within a liquid-nitrogen-cooled quartz dewar.

The luminescence lifetimes were measured by multi-channel scaling following excitation into the lowest-energy absorpton band using a microsecond pulsed xenon lamp. The emitted light was detected at 90° using a Peltier-cooled R928 PMT after passage through a monochromator.

The luminescence of singlet oxygen sensitised by the complex in air-equilibrated CH_2Cl_2 solution was detected using a Peltier-cooled Hamamatsu H10330B-75 near-infrared PMT module, following excitation at 400 nm. Interference from second-order diffraction of the light emitted by the complex was eliminated using a Schott® glass RG850 longpass filter between sample and detector. The quantum yield of singlet oxygen formation was determined using 1-*H*-phenalen-1-one (perinaphthenone) as the standard, for which $\Phi(^1\Delta_g\ O_2)$ = 0.98 under the same conditions.[45] For the sample and for the standard, the integrated emission intensity of $^1O_2$ over the range 1225 – 1340 nm was plotted against the fraction of light, *f*, absorbed for three solutions for which $0.1<f<0.3$, and the relative quantum yield obtained from the ratio of the best-fit gradients of the plots.[46]

The circularly polarized luminescence (CPL) measurements were performed using a home-built CPL spectrofluoropolarimeter (with the help of the JASCO company). The samples were excited using a 90° geometry with a Xenon ozone-free lamp 150 W LS. The following parameters were used: emission slit width ≈ 2 mm, integration time = 4 sec, scan speed = 50 nm/min, accumulations = 5. The concentration of all the samples was ~10^{-5} M. Excitation of the samples were performed at 350 nm. The solutions were carefully deaerated.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

Acknowledgements

We acknowledge the Ministère de l'Education Nationale, de la Recherche et de la Technologie, the Centre National de la Recherche Scientifique (CNRS), the CNRS (Chirafun network), the ANR (12-BS07-0004-METALHEL-01 and ANR-16-CE07-0019-01-HEL-NHC), and the Rennes-Durham Associated International Laboratory (IAL MMC) for financial support. Part of this work has been performed using the PRISM core facility (Biogenouest, UMS Biosit, Université de Rennes 1 - Campus de Villejean-35043 RENNES Cedex, FRANCE).

Author Contribution Statement

A. Macé, N Hellou, J Hammoud, C. Martin and E. S. Gauthier performed the synthetic work. L Favereau and J. Crassous measured the chiroptical properties. T. Roisnel performed the X-ray analysis. E. Caytan performed the NMR analysis. N. Vanthuyne performed the HPLC separation. J. A. G. Williams evaluated the photophysics. G. Nasser, F. Berrée, J. A. G. Williams, B. Carboni and J. Crassous contributed to the discussion of the scientific project and wrote the manuscript.

Note

[#] CCDC 1894800, contains the supplementary crystallographic data for complex **C**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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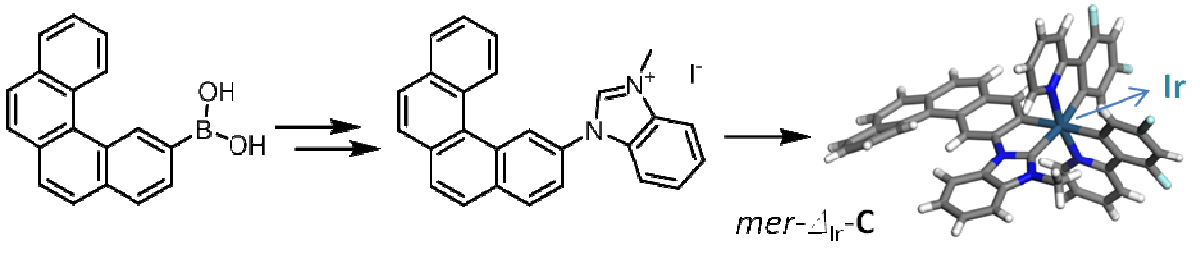

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