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Chiral Organometallic Complexes derived from Helicenic N-Heterocyclic Carbenes (NHCs): Design, Structural Diversity, Chiroptical and Photophysical Properties

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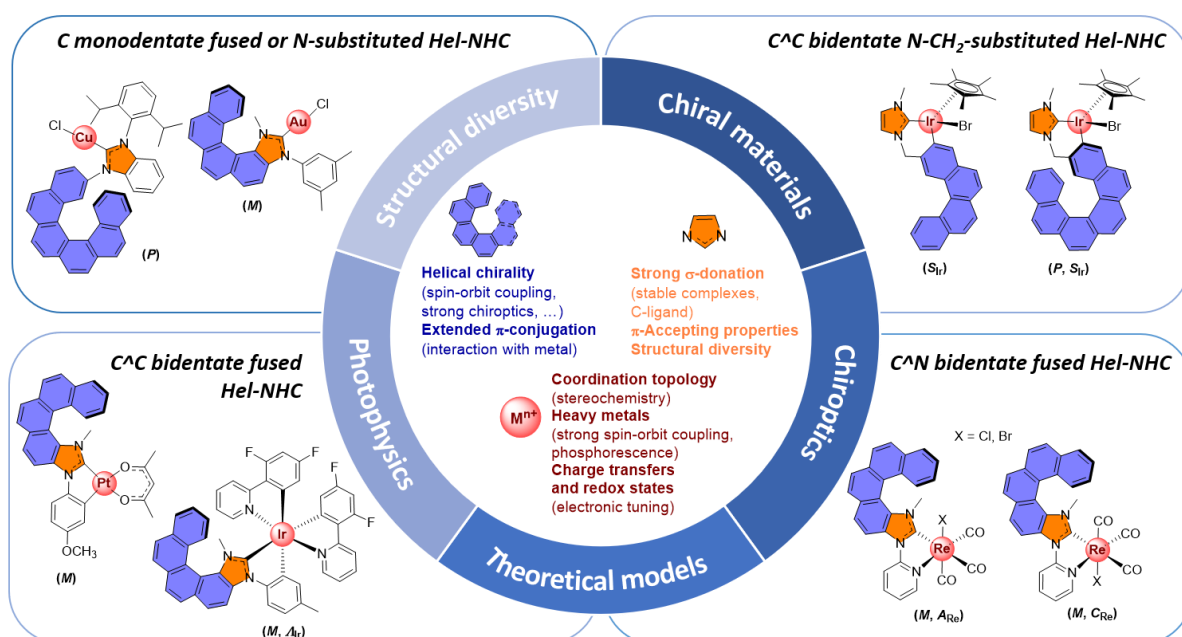
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- **Conspectus**

Recently, helicene derivatives have emerged as an important class of molecules with potential applications spanning over asymmetric catalysis, biological activity, magnetism, spin filtering, solar cells, and polymer science. To harness their full potential, especially as emissive components in circularly polarized organic light-emitting diodes (CP-OLEDs), generating structural chemical diversity and understanding the resulting photophysical and chiroptical properties is crucial. In this Account, we shed light on the chemical engineering combining helicene and N-heterocyclic carbene (NHC) chemistries to create transition metal complexes with unique architectures and describe their photophysical and chiroptical attributes. The σ -donating and π -accepting capabilities of the helically chiral π -conjugated NHCs endow the complexes with remarkable structural and electronic features. These characteristics manifest in phenomena such as chirality induction, very long-lived phosphorescence, strong chiroptical signatures (electronic circular dichroism and circularly polarized luminescence).

We describe the different classes of ligands primarily developed in our group, by classifying them according to their connection between the helicenic moiety and the imidazole precursor. This connection is essential in determining the degree of π -conjugation and characterizing the emissive state. We comprehensively discuss 6-coordinate, 4-coordinate, and 2-coordinate complexes, delving into their structural nuances and examining how the interplay between metals and auxiliary ligands shapes their photophysical properties, with interpretations enriched by DFT calculations. Helicenes are known to promote intersystem crossing thanks to strong spin-orbit coupling while metals offer robust frameworks leading to a variety of molecular architectures with specific topologies together with distinct excited state properties. The electronic configurations and energy levels of ligand and metal orbitals thus significantly modulate the photophysical and chiroptical behaviors of these complexes. In-depth analysis of chiroptical properties, notably electronic circular dichroism and circularly polarized luminescence, emphasizes the influence of different stereogenic elements on the chiroptical responses across various energy ranges with appealing 'match - mismatch' effects. Finally, we describe future prospects of helicene NHCs, particularly in the context of emerging research on cost-effective and abundant transition metals for materials science and for photocatalysis. Indeed, the inherent long-lived MLCT, excited state delocalization, structural rigidity, and intrinsic chirality of these complexes present intriguing avenues for future investigations.



Key references

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- Gauthier, E. S.; Hellou, N.; Caytan, E.; Fré, S. D.; Dorcet, V.; Vanthuyne, N.; Favereau, L.; Srebro-Hooper, M.; Williams, J. A. G.; Crassous, J. Triskelion-Shaped Iridium-Helicene NHC Complex. *Inorg. Chem. Front.* **2021**, 8, 3916–3925.⁴ *Our report on the first transition metal complex surrounded by three helicenic ligands.*

Introduction

N-heterocyclic carbene (NHC) transition-metal complexes (TMCs) have undergone rapid development in the last decades due to their important applications in catalysis, medicinal chemistry, and materials science.⁵ Notably, the high structural modularity of NHCs has enabled to design a large variety of chiral architectures, giving access to highly stereoselective organometallic catalysts.⁶ Furthermore, chiral NHC-TMCs may combine chiroptical activity with other desired properties such as emission, electroactivity and high stability, which make them attractive candidates as multifunctional optoelectronic materials.⁷ Nevertheless, studies exploring the chiroptical properties of NHC-TMCs are still rare.⁸ [*n*]Helicenes are formed of *n* ortho-fused (hetero)aromatic rings and exhibit an extended π -conjugation with helical topology and unique strong chiroptical properties, such as high molar rotations (MRs),[§] intense electronic circular dichroism (ECD) and high circularly polarized emission (CPL).⁹ The benchmark photophysical and chiroptical properties of parent organic carbo[6]helicene are depicted on Figure 1. In the last two decades, our group has demonstrated how the coordination of helicenic ligands to transition metals can lead to metallo-chiral organic species with diverse topologies and unique chirality-related physico-chemical properties.¹⁰ We have recently applied this strategy to develop the chemistry of helicene-based NHCs. Herein, we describe the synthesis of helicenic NHC-TMs we have developed, with a special focus on their structural diversity and stereochemical features. Diverse types of helical ligands combined with different metal centers yielded numerous appealing molecular systems. These compounds readily crystallized into single crystals, thus enabling analysis of their topology and structural features by X-ray crystallography. Great insights were also accessed via experimental 2D NMR combined with theoretical calculations. Thanks to their high stability and neutral charge, they could be resolved into pure enantiomers by chiral HPLC separations. The photophysics and chiroptical activity of the pure compounds were then thoroughly characterized, revealing intriguing aspects such as long-lived phosphorescence, which could be interpreted with the help of time-dependent DFT (TDDFT) calculations. This Account focuses on our achievements in the domain of helicenic NHC-TMCs that we have prepared and studied since 2016.

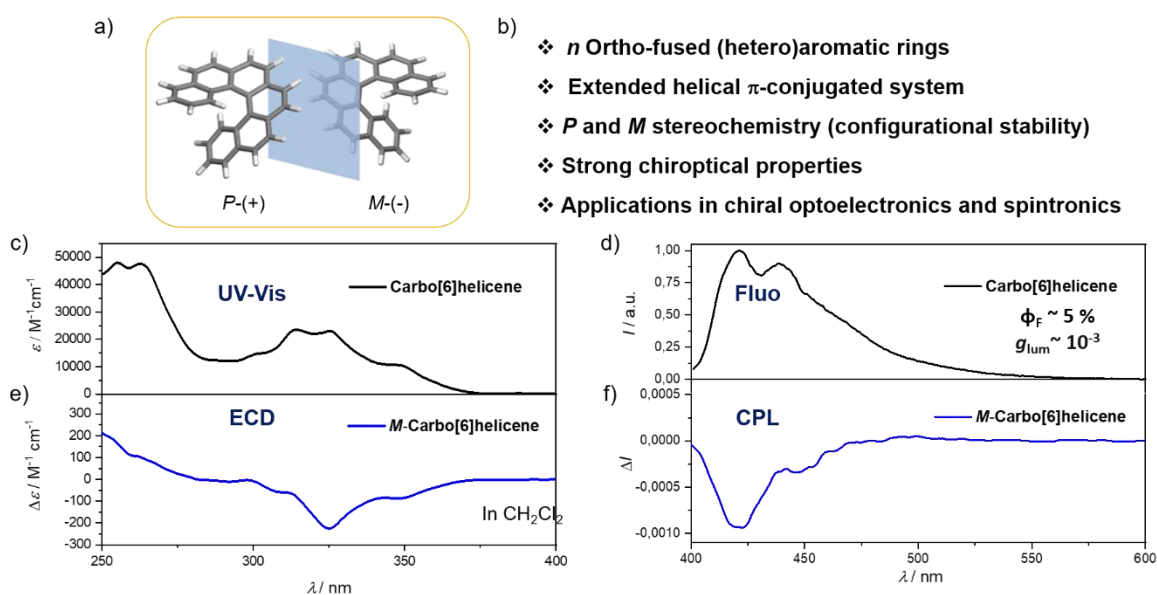


Figure 1. a) Mirror-imaged *P*-(+) and *M*-(*-*) enantiomers and b) general features of parent carbo[6]helicene. Photophysical (c) UV-vis and d) fluorescence) and chiroptical (e) ECD and f) CPL) properties of the *M* enantiomer. The fluorescence quantum yield and dissymmetry factor are also given.⁹

1. Synthesis, structural diversity and stereochemical features of helicenic NHC-TMCs

The structural diversity in the NHC ligand containing helicene backbone is depicted in Schemes 1-3. Those were prepared using classical methodologies. While the pentahelicenic imidazolium salts are difficult to resolve enantiomerically, the stable and neutral organometallic species could be obtained upon complexation and well-separated into enantiomers by classical chiral HPLC (*ee*'s 92-99%). On the other hand, the hexahelicenic systems are configurationally stable and their corresponding enantiopure imidazole and imidazolium derivatives could be synthesized using appropriate enantiopure starting hexahelicenes, thus giving the possibility to directly obtain enantiopure complexes. Thanks to π - π stacking interactions, these compounds readily crystallized into single crystals, thus enabling analysis of their structural features by X-ray crystallography. Invaluable insights were also obtained via experimental 1D and 2D-NMRs complemented with theoretical calculations that we will discuss in the next section.

1.1. Heteroleptic iridium complexes from structurally diverse helicenic NHC ligands

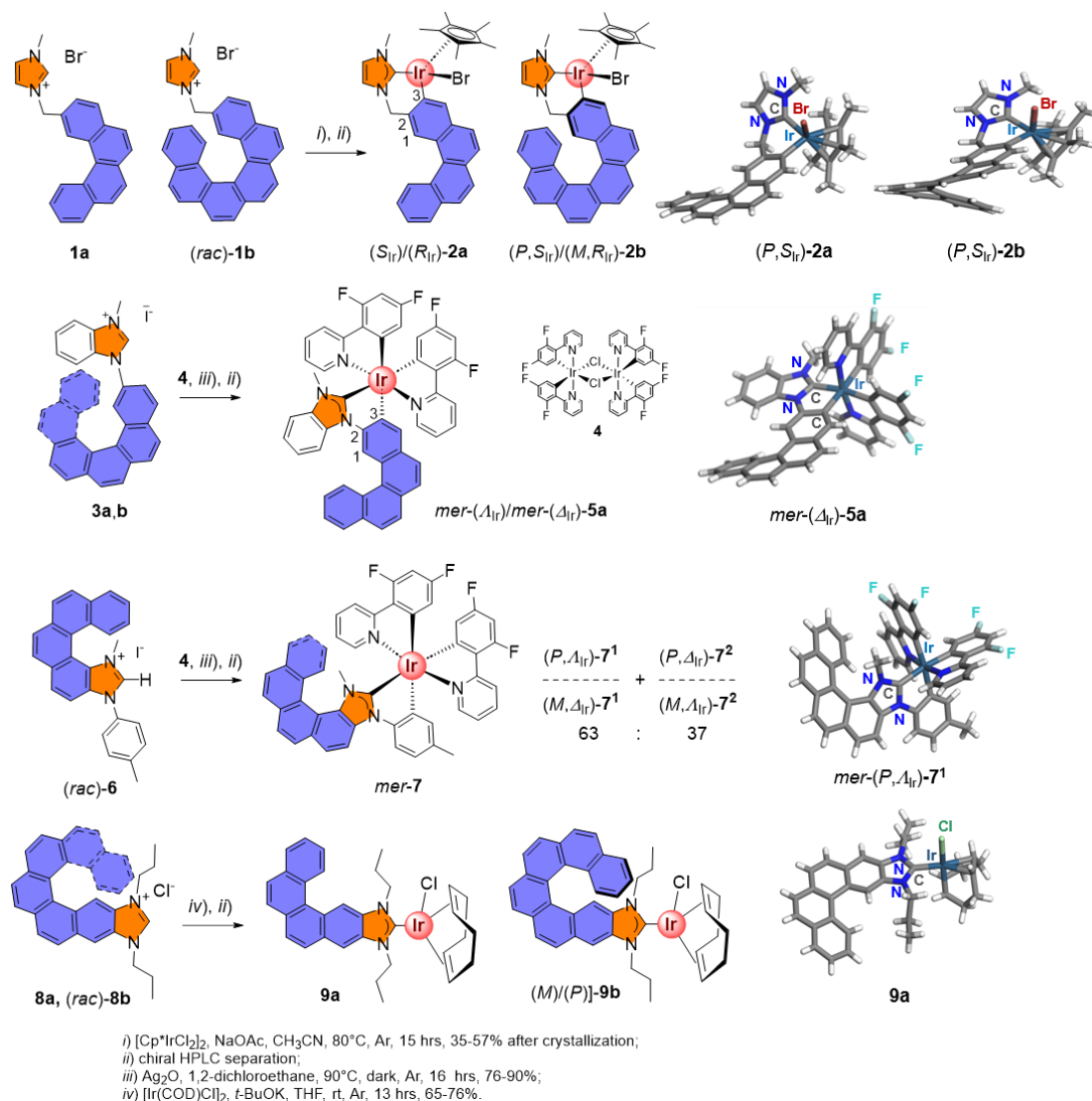
Scheme 1 depicts the diversity of heteroleptic d⁶-iridium-based NHC-TMCs our group has been able to generate. Helicenic scaffolds have been implemented at different positions of imidazolium salts, such as at *N* atom in tetra- and hexahelicene-methylene-imidazolium bromides **1a,b**, in [4]helicene-2-benzimidazolium iodide **3**, or totally fused within the imidazolium cycle, like in pentahelicenic imidazolium iodide **6** and in [4,6]helicene-fused imidazolium chlorides **8a,b**. These *N*-heterocyclic compounds behaved either as bidentate (*C*[^]*C*) or monodentate (*C*) proligands and their corresponding Ir^{I,III} complexes were obtained using classical coordination conditions.¹ Using NMR analysis, we could confirm, in all cases, that an Ir^{III}-carbene bond was formed, while additional insights into their structure and

stereochemical features were provided by X-ray crystallographic analysis. As depicted on Scheme 1, compounds **2a** and **2b** showed cyclometallation at position 3 and a 6-membered iridacycle with a stable boat-like conformation. In the solid state, two stereogenic elements were found for **2a**, as only one (M,R_{Ir}) and (P,S_{Ir}) enantiomeric pair; in solution, the [4]helicene fragment was not configurationally stable and only the (R_{Ir})/(S_{Ir})-Ir stereogenic center was found. Interestingly, [6]helicenic analogue (*rac*)-**2b** spontaneously resolved into homochiral crystals ($P2_12_12_1$ space group), with only the (P,S_{Ir})/(M,R_{Ir}) homochiral species observed, meaning that the helical chirality of the ligand governed the chirality at the tetrahedral Ir center. Similar stereochemical control and stable conformation of the iridacycle was observed in solution.

The cycloiridiated complex **5a** was synthesized following classical transmetallation reaction of an *in situ* obtained NHC-silver(I) intermediate which then reacted with *trans*-[Ir(dfppy)₂(μ -Cl)₂] complex **4** (dfppy = 2-(2,4-difluorophenyl)-pyridyl).¹¹ As in the previous example, complex **5a** displayed cyclometallation at helicenic position 3 giving a 5-membered iridacycle, with almost coplanarity between the C^{carbene}-Ir-C³ plane and the phenyl ring of the helicene (Scheme 1). (*Rac*)-**5a** showed a pseudo-octahedral geometry around the (Δ_{Ir})/(Λ_{Ir}) chiral Ir^{III} center within a meridional (*mer*) arrangement dictated by the *trans* configuration of **4**. Here again, [4]helicenic part displayed a helicity in the solid state, which was not configurationally stable in solution. Note that upon coordination to iridium, the π -system was elongated to seven fused aromatic rings, including the carbenic ring. Overall, these features had a direct impact on the photophysical properties of the molecule (*vide infra*).

Fused helicenic imidazolium salts **6** and **8a,b** could be readily prepared from 1,2-diamino-[4]helicene, [2,3]diisopropylamino-[4]helicene and its [6]helicenic analogue, respectively.^{2,12} The heteroleptic cycloiridiated complexes **7**^{1,2} bearing similar features as for **5** were prepared from helically fused imidazolium salt **6** (Scheme 1).² The cyclometallation appeared diastereoselective (2:1 **7**¹/**7**² diastereoisomeric ratio) and X-ray analysis revealed that (M,Δ_{Ir})/(P,Λ_{Ir})-**7**¹ was the major diastereomer and (P,Δ_{Ir})/(M,Λ_{Ir})-**7**² the minor one. Systems **7**^{1,2} were actually the first reported ones bearing a chiral, purely helical, fused *N*-heterocyclic carbenic ligand. Heteroleptic Ir^I complexes **9a,b** bearing cyclooctadiene (COD), chloro ligands and monodentate [4,6]helicenic NHCs were prepared upon reaction of **8a,b** with [Ir(COD)Cl]₂ in the presence of *t*-BuOK.¹² The X-ray structure of racemic **9a** ($P-1$ centro-symmetric space group, Scheme 1) showed a pseudotetrahedral geometry around the iridium center. The [4]helicenic part had a helicity (27°) in the solid state, but was not configurationally stable in solution. Specific stereochemical features were observed for **9b**: a set of four signals was obtained by HPLC separation, corresponding to enantiomeric pairs (M)-(-)/(P)-(+)-**9b**¹ and (M)-(-)/(P)-(+)-**9b**². NOESY experiments revealed two positions adopted by the COD ligand, one directed towards the helical moiety and one on the opposite direction, with an interconversion barrier between the two estimated to be 104 kJ.mol⁻¹ at 25°C, so that exchange took only a few hours at ambient temperature. Note that similar HelNHC-Ir(COD)Cl complexes were prepared from pentahelicenic proligand (see **17** in Scheme 3) as intermediate of HelNHC-Ir(CO)₂Cl complex, whose IR spectroscopic characteristics (CO stretching band) enabled to evaluate the stronger π -acidic character of such extended helically fused NHC ligand, as

compared to more classical ones such as benzimidazolylidenes.¹³ Isostructural rhodium(I) analogues of **9a,b** were also prepared.¹²

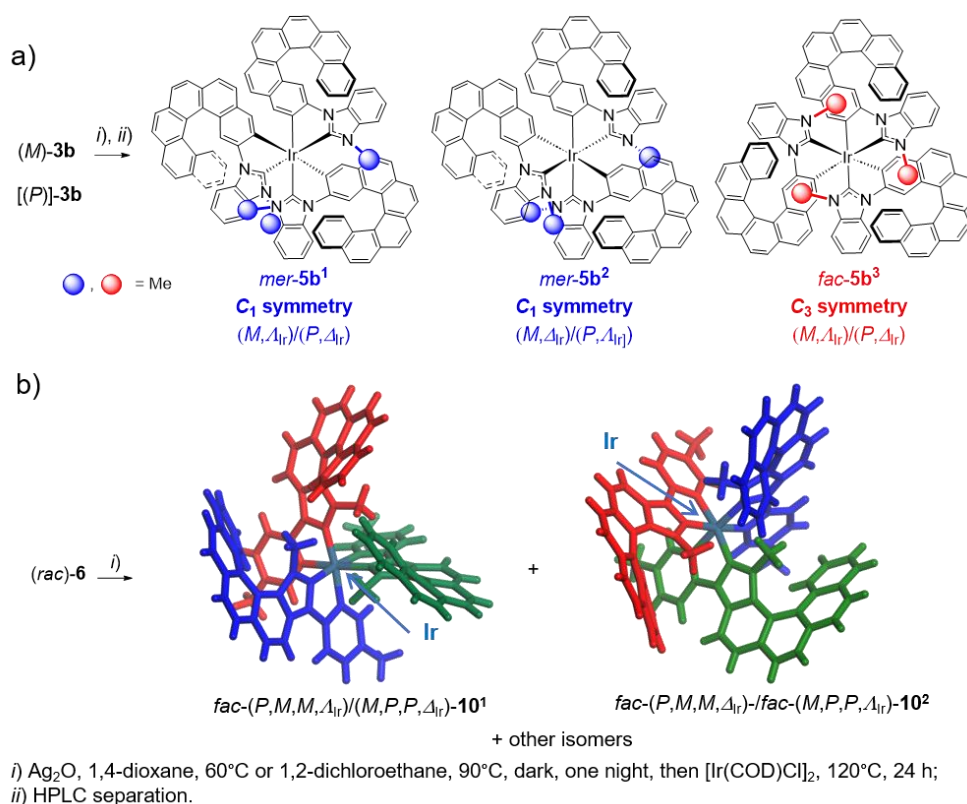


Scheme 1. Synthesis of Ir complexes bearing one helicene at different positions of the NHCs (*N*-substituted or fused), and their X-ray crystallographic structures. Only one stereoisomer shown.

1.2. Homoleptic iridium-based multihelicenic architectures

In all above examples, one helical NHC is coordinated to one Ir center. Actually, it appeared rather challenging to install more than one helical ligand around one metal center for obvious steric reasons. Pleasingly, starting from enantiopure ligand (*P*)/(*M*)-**3b**, we were able to prepare homoleptic triskelion shaped iridium complexes such as **5b** and **10** (Scheme 2).⁴ Due to the helical chirality of the three ligands, the *fac/mer* and $(\Delta_{\text{Ir}})/(\Lambda_{\text{Ir}})$ of the Ir center, many stereoisomers were produced and three different stereoisomers (2 meridional and 1 facial) were isolated and identified. Using a similar procedure, complex (*rac*)-**10** was obtained from (*rac*)-**6**. The tris-carbenic cycloiridiated $\text{Ir}(\text{C}^{\wedge}\text{C})_3$ with its triskelion topology was ascertained by X-

ray crystallography. As depicted on Scheme 2b, two isomeric structures could be isolated, namely *fac*-(*P,M,M*, Δ_{Ir})/(*M,P,P*, Δ_{Ir})-**10**¹ and *fac*-(*P,M,M*, Δ_{Ir})/(*M,P,P*, Δ_{Ir})-**10**².



Scheme 2. a) Synthesis and stereochemical structures of the prepared chiral *mer* and *fac* complexes **5b**¹⁻³. b) X-ray structures of two *fac* isomers of (*rac*)-**10**^{1,2} (only one enantiomer shown) synthesized using ligand (*rac*)-**6**.

1.3. Platinum and rhenium complexes bearing helicene-NHC ligands

Aside from Ir center which enabled us to establish proofs of concepts in the generation of helicene-based NHC-TMCs, many other metals have been successfully tested (see Scheme 3). Following a similar synthetic route, cycloplatinated complexes (*P*)/(*M*)-**12a,b** bearing a pentahelicene *C*[^]*C* ligand and either one acetylacetonate (acac, **12a**) or dibenzoylmethane anion (dbm, **12b**) were prepared.¹⁴ X-ray analysis of the d⁸-Pt complex **12b** ascertained the carbenic structure. The Pt^{II} center being square planar, it is not a stereogenic element and complexes **12a,b** only exist as enantiomeric pairs that could be readily resolved by chiral HPLC separation.

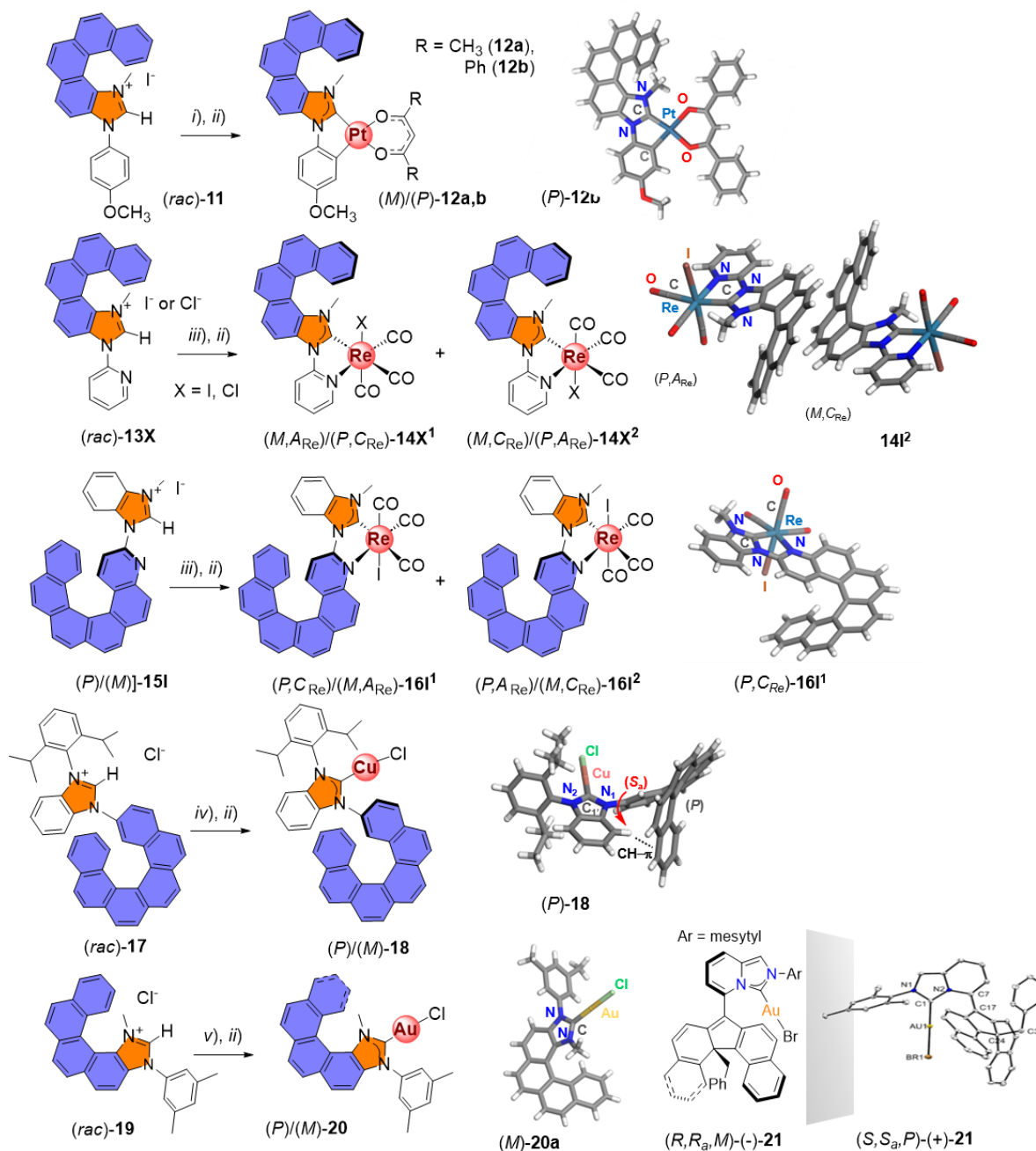
Another interesting case was the synthesis of rhenium complexes which were readily obtained by first preparing 3*N*-(2-pyridyl)-[5]helicene-imidazolium iodide or chloride salts (*rac*)-**13X** (**X** = **I**, **Cl**) then reacting these helical *C*[^]*N* bidentate proligands with ReCl(CO)₅ under classical conditions (see Scheme 3) to yield **14I**^{1,2} and **14Cl**^{1,2}, respectively.³ Both **14I** and **14Cl** contain two stereogenic elements: the [5]helicene – which is configurationally stable thanks to the methyl group at the N¹ atom – and the Re(I) center, which can adopt *A/C*

stereochemistry (see Scheme 3). Consequently, mixtures of diastereomeric complexes (M, A_{Re})-**14X¹** and (M, C_{Re})-**14X²** are formed {together with their (P, C_{Re}) and (P, A_{Re}) mirror images}. These d⁶-Re(I) compounds existed as diastereoisomers (in around 85:15 and 65:35 ratios for **14I^{1,2}** and **14Cl^{1,2}**, respectively). Their structure was evidenced by X-ray crystallography of the minor diastereoisomer **14I²** ($P2_1/n$ centrosymmetric space group) corresponding to the (M, C_{Re})/(P, A_{Re}) enantiomeric pair, as depicted in the heterochiral assembly in Scheme 3. The Re^I ion adopts a slightly distorted pseudo-octahedral geometry, with the three carbonyl groups being *fac*-oriented around the metal. The equatorial planes are defined by the chelating pyridine-NHC ligand and two carbonyls, with the third carbonyl and the iodine atom occupying the axial positions. The iodine points in the opposite direction to the helicene moiety in **14I²**, while in the major diastereomer (M, A_{Re})/(P, C_{Re})-**14I¹**, it is directed towards the helicene core. The helicenic moiety displays a helicity angle of 51°, typical for [5]helicenes and consistent with those of cycloiridiated complex **7¹** bearing a similar [5]helicene-NHC ligand. The structure also indicated extended π -conjugation over the whole molecule and efficient electronic interaction between the bidentate [5]helicene-NHC-pyridyl ligand and the metal, as corroborated by isosurfaces of frontier molecular orbitals (MOs, *vide infra*). Furthermore, neutral and stable complexes **14X^{1,2}** were readily obtained in diastereomerically and enantiomerically pure forms *via* HPLC over chiral stationary phases. Within the same Re^I series, it was interesting to test whether the helical unit could be placed as a substituent of a benzimidazolium *N*-atom, as in the case of aza[6]helicene **15I**. Thus diastereomeric pair (P, C_{Re})-**16I¹** and (P, A_{Re})-**16I²** was obtained from (*P*)-**15I** and the structure of the major isomer (P, C_{Re})-**16I¹** was ascertained by X-ray crystallography (see Scheme 3).¹⁵

1.4. Copper and gold complexes bearing monodentate helicenic NHC ligands

The preparation of closed-shell racemic d¹⁰-NHC-copper(I) and gold(I) chloride complexes was also investigated. Reaction of [6]helicene-benzimidazolium salt (*rac*)-**17** with copper(I) chloride yielded (*rac*)-**18** which appeared air-stable thanks to the steric hindrance of both helicenic and 2,6-diisopropylbenzene substituents at the N atoms.¹⁶ The racemic Cu(I) complex, neutral and chemically stable, was then easily resolved by chiral HPLC separation. X-ray crystallography of (*P*)-**18** ($P2_12_12_1$ space group) confirmed the typical of two-coordinate NHC-Cu-Cl complexes, with a nearly linearity around the Cu^I (see Scheme 3). The [6]helicene moiety displays a typical helicity of 63.5° while the diisopropylphenyl group is almost perpendicular to the benzimidazolyliene ring. It is also interesting to note that two stereogenic elements were found in the solid state of **18**, *i.e.* the (*P*) helical chirality originating from the [6]helicene unit and the axial chirality with the presence of a dihedral angle of *c.a.* +130° between the NHC and the attached terminal ring of the helicene. The (*P*) chirality of the helicene thus dictates the (*S_a*) axial chirality and this chiral induction is reinforced by the presence of a CH- π interaction between one CH of the benzimidazole ring and the terminal phenyl ring of the helicene (Scheme 3, H-centroid distance of 2.628 Å). This (M, R_a)/(P, S_a)-**18** enantiomeric pair of diastereoisomers was also found stable in solution. In the same manner, reaction of pentahelicene fused imidazolium salt (*rac*)-**19** under classical conditions gave access to air stable gold(I) complex (*rac*)-**20**.¹³ The latter crystallized in centrosymmetric $C2/c$ space group and displayed a helicity close to 50° with is nearly linear geometry around the gold(I) center,

as in typical two-coordinate NHC-Au(I) complexes. No metallophilic interactions were observed, probably due to steric congestion. The chloro ligand could further be exchanged by either phenyl-acetylide or the carbazolide ones. In 2022, in collaboration with César and coworkers, a new class of gold complexes (**21** in Scheme 3) bearing central, axial and helical chirality within the same architecture was synthesized and employed as enantioselective catalyst in the benchmark cycloisomerization of 1,6-enynes (*ee*'s up to 90%).¹⁷



Scheme 3. Synthesis of Hel-NHC complexes with diverse transition metals, and their corresponding X-ray crystallographic structures. Only one stereoisomer shown.

2. Photophysical and chiroptical properties

The great diversity of complexes prepared in enantiomerically and diastereomerically pure forms gave us the big opportunity to examine in details their photophysical and chiroptical responses: not only what were the contributions of each component, *i.e.* hel-NHC ligand and metal center, but also how the helical NHC ligand was interacting with the coordinated metal ions and what were the consequences on their properties. These fundamental aspects revealed intriguing features that may be of great interest for developing applications in chiral materials science.

2.1. Cycloiridiated helicene-methylene-NHC complexes: contribution of the helical NHC and of the metal center on the electronic circular dichroism spectra

The chiroptical properties, namely ECD and MR[§] values of firstly prepared **2a** and **2b** enantiomers were studied.¹ The mirror-image ECD spectra of "chiral at Ir" complex **2a** depicted on Figure 2 were found relatively weak, with $\Delta\epsilon$ values lower than $\pm 36 \text{ M}^{-1} \text{ cm}^{-1}$. The MR values were also low ($[\phi]_D^{23} = \pm 230$, $C 1.8 \cdot 10^{-3} \text{ M}$, CH_2Cl_2 , within the experimental errors). The (*S*_{Ir})-(+ and (*R*_{Ir})-(-) absolute configurations were determined from X-ray structure of enantiopure (+)-**2a** which crystallized in the *P2*₁*2*₁*2*₁ space group. Comparatively to **2a**, the enantioenriched (*M,R*_{Ir})- and (*P,S*_{Ir})-**2b** samples exhibit intense mirror-image ECD spectra in CH_2Cl_2 nm, with $\Delta\epsilon$ values as high as $\pm 164 \text{ M}^{-1} \text{ cm}^{-1}$ and strong molar rotation values ($[\phi]_D^{23} = \pm 12350$, $C 1.1 \cdot 10^{-4} \text{ M}$, CH_2Cl_2), thus highlighting the importance of the [6]helicenic component for generating strong chiroptical responses in the transmission and absorption regimes.

ECD of (*P,S*_{Ir})-**2b** was calculated by TD-DFT (Figure 2b). The MO-pair analysis of the intense excitations revealed a strong involvement of the Ir^{III} orbitals and carbenic π -system in the ECD-active transitions. Transitions with metal-to-ligand (ML), ligand-to-metal (LM) and ligand-to-ligand (LL) CT character were clearly obtained. These excitations are responsible for the pronounced low-energy tail of the ECD spectrum of **2b** and account for the noticeable differences between the calculated spectrum of (*P,S*_{Ir})-**2b** *versus* that of the NHC-helicene ligand (*P*)-**2b'** which mainly provides pure $\pi-\pi^*$ helicene character. Overall, the spectral analysis showed that the 6-membered iridacycle enabled electronic coupling between the metal center and the helicenic NHC ligand. This work was the first study highlighting the NHC involvement in the chiroptical properties of a chiral NHC transition metal complex.¹

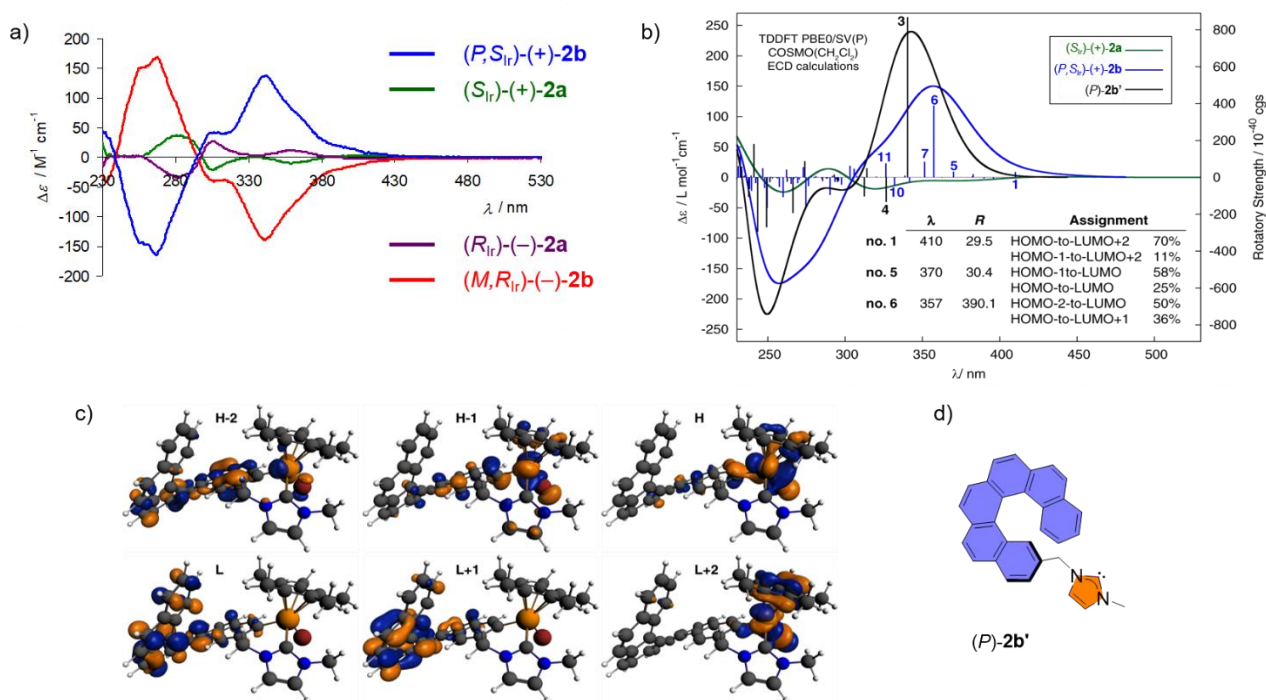


Figure 2. a) ECD spectra of $(R_{Ir})/(S_{Ir})$ -**2a** and $(P,S_{Ir})/(M,R_{Ir})$ -**2b** in CH_2Cl_2 at rt. b) Comparison of the simulated ECD spectra of (S_{Ir}) -**2a**, (P,S_{Ir}) -**2b** and its parent NHC-helicene ligand (P) -**2b'**. Calculated excitation energies and rotatory strengths indicated as ‘stick’ spectra. Selected dominant excitations and occupied-to-unoccupied MO pair contributions of the (P,S_{Ir}) -**2b**. Rotatory strength R in 10^{-40} cgs. c) Selected MOs involved in the ECD-active bands of **2b**. H: HOMO, L: LUMO. d) Chemical structure of (P) -**2b'**.

2.2. Long-lived CP-phosphorescent cycloiridiated helicene-NHC complexes

Cyclometallated iridium(III) complexes are often highly luminescent in solution, emitting from triplet states. The archetypal systems *fac*- $\text{Ir}(\text{ppy})_3$ and *cis*- $[\text{Ir}(\text{ppy})_2(\text{bpy})]^+$ have been complemented over the past two decades by a large array of derivatives, including systems that feature carbenic $C^{\wedge}C$ coordinating ligands in place of one or more of the $N^{\wedge}C$ ligands.¹⁸ The replacement of the heterocyclic unit by a carbene typically attenuates the π acceptor nature, leading to the destabilization of metal-to-ligand charge-transfer excited state levels and hence to blue shifted absorption and emission. In this context, the case of cycloiridated complexes **7**^{1,2} appeared highly interesting since it revealed new features in these types of complexes thanks to the presence of the helicene.² As depicted on Figure 3c, DFT calculations highlighted 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. Bonding analysis highlighted the dative NHC-metal bond with $\text{NHC} \rightarrow \text{Ir}$ σ -donation and $\text{Ir} \rightarrow \text{NHC}$ back-donation components, typical for carbenic ligands, but with the π -back-bonding clearly enhanced due to the extended π -helicene system. This is in accordance with the experimental results obtained from the IR studies of the $\text{Ir}(\text{CO})_2\text{Cl}$ complexes with pentahelicenic monodentate ligands (*vide supra*).¹³ These electronic features may account for the good stability and unprecedented photophysical and (chir)optical properties of **7**^{1,2}. The mirror-imaged ECD spectra depicted in Figure 3a revealed that (P,A_{Ir}) -**7**¹ and (P,A_{Ir}) -**7**² possess

ECD bands at similar wavelengths but some of them having opposite signs (at ca. 275 and 305 nm). Effects of both Ir and helicene-NHC chirality was further demonstrated by a comparison with model complex **A** (see Figure 3d), showing similar but much less intense ECD pattern. The experimental MRs at 436 nm also reflected differences between the two epimers ((P, Δ_{Ir}) -**7¹**: +16520; (P, Δ_{Ir}) -**7²**: 2170), showing that the contribution of the (Δ_{Ir}) center compensates and even surpasses the one from the (P) -[5]helicene-NHC.

The efficient interaction between the π -helical NHC and Ir(III) was also reflected in the emission properties of **7^{1,2}**, with both complexes displaying vibrationally structured light-green phosphorescence at 525 nm and emission quantum yields of ca. 9-13%. The **7^{1,2}** emission was red-shifted compared to that of the model complex **A** which displayed a typical blue-green phosphorescence at 498 nm. Particularly striking was the extremely long phosphorescence lifetimes of $\sim 300 \mu\text{s}$ observed for **7^{1,2}**, much longer than values of $1 \mu\text{s}$ typically recorded for tris-cyclometalated Ir^{III} complexes, or the $3.1 \mu\text{s}$ observed for **A**. The measured lifetimes were amongst the longest reported for cycloiridiated systems and are due to the extended π -conjugation in the helical NHC ligand and its high spin-orbit coupling. As a result, the luminescence of these complexes is extremely sensitive to oxygen and efficient sensitization of singlet oxygen is anticipated.¹⁹ The CPL spectra of enantiopure stereoisomers of **A** and **7^{1,2}** in deoxygenated CH_2Cl_2 samples were also interesting to examine (Figure 3b). Each enantiomeric pair displayed mirror-image CP phosphorescence with dissymmetry factors $g_{\text{lum}}=2(I_{\text{L}}-I_{\text{R}})/(I_{\text{L}}+I_{\text{R}})$ of $+9 \times 10^{-4}$ at 493 nm for (Δ_{Ir}) -**A**, and of $+3.7 \times 10^{-3}$ and $+1.5 \times 10^{-3}$ at 530 nm for (P, Δ_{Ir}) -**7¹** and (P, Δ_{Ir}) -**7²** respectively, 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, Δ_{Ir}) -**7¹** vs. (P, Δ_{Ir}) -**7²** ('match/mismatch' effect). Manipulating the Ir^{III} stereochemistry thus enabled the CPL response to be tuned.

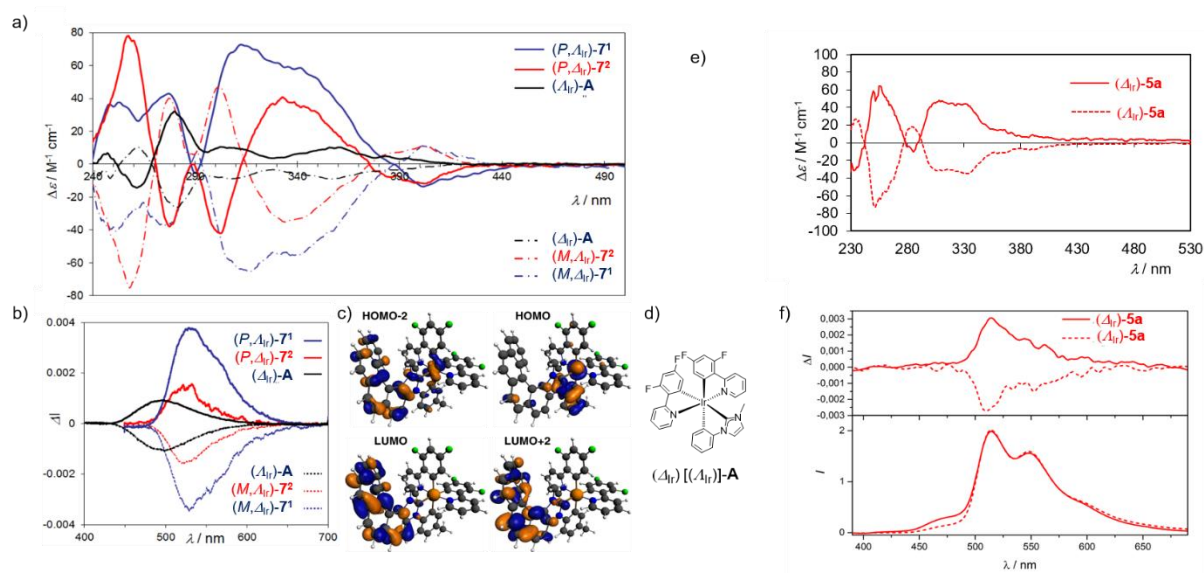


Figure 3. a) ECD and b) CPL spectra of (P, Δ_{Ir}) -**7¹** and (P, Δ_{Ir}) -**7²**, of their mirror-images (M, Δ_{Ir}) -**7¹** and (M, Δ_{Ir}) -**7²**, and of model (Δ_{Ir}) / (Δ_{Ir}) -**A**. c) Selected MOs of (P, Δ_{Ir}) -**7¹**. d) Structure of (Δ_{Ir}) [(Δ_{Ir})]-**A**.

model **A**. e) ECD, f) emission and CPL spectra of (Δ_{Ir})-(-) and (Δ_{Ir})-(+)-**5a**. All spectra measured at rt in (deaerated) CH_2Cl_2 .

These results are interesting to compare to those of **5a** which displays a vibrationally structured phosphorescence spectrum between 510 and 660 nm, with 5% quantum yield and 140 μs lifetime.¹¹ These characteristics are attributed to the extended π -conjugation of the helicene, and an excited state that is much more localized on the π -system, although with some contribution from ³MLCT-type transitions. As a result, efficient singlet oxygen production was observed.¹⁹ Remarkably, **5a** remained highly luminescent in the solid state, with a strongly red-shifted emission around 615 nm but still well-structured, and luminescence lifetime of 960 μs ! Complexes (Δ_{Ir})- and (Δ_{Ir})-**5a** were also CPL-active (Figure 3e), with respective maximum g_{lum} values of -2.6×10^{-3} and $+3.1 \times 10^{-3}$, *i.e.* of similar orders as those of model **A** and diastereomers **7**^{1,2}.

2.3. Long-lived CP-phosphorescent helicene-NHC rhenium complexes

Thanks to their heavy rhenium atom exhibiting strong spin-orbit coupling, rhenium complexes are known to be efficient phosphors. The ECD spectra of enantiopure **14I**^{1,2} and **14CI**^{1,2} with *P* helices in CH_2Cl_2 are depicted on Figure 4a.³ The systems with the same stereochemistry [(*P*, C_{Re}) for **14I**,**CI**¹; (*P*, A_{Re}) for **14I**,**CI**²] appeared to display very similar fingerprints but with some bands exhibiting different intensities. Epimeric species (**14I**¹ vs. **14I**² and **14CI**¹ vs. **14CI**²) showed differences in the region where the Re stereogenic center is mostly involved (above 360 nm). All this reflects the impact of the rhenium chirality and 'match/mismatch' effect on the overall chiroptical activity. The computed ECD spectra displayed on Figure 4b enabled assignments of the bands, the most intense calculated excitations (see Figures 4c and d) being qualitatively the same in each case, *i.e.* mixtures of MLCT/XLCT/ILCT and IL π - π^* transitions, when going from longest to shortest wavelengths. Overall, the metal, helicene and NHC units were efficiently communicating and involved in the main transitions.

Chloro helicene-NHC-Re diastereoisomers **14CI**¹ and **14CI**² displayed moderately intense vibronically structured green phosphorescence at 520 nm in deaerated CH_2Cl_2 solution at rt. The emission was found red-shifted compared to the model complexes without helicenic ligand. More importantly, the phosphorescence lifetimes τ_{phos} were 4000-6000 times greater in the helicene complexes, from 0.1 μs for models to several hundreds of μs for **14CI**^{1,2}, corresponding to the longest ever reported for such neutral rhenium complexes. Interestingly, subtle differences were found in τ_{phos} between the diastereoisomers. The **14CI**¹ enantiomers (*M*, A_{Re})/(*P*, C_{Re}) had lifetimes around 700 μs , whereas for the (*M*, C_{Re})/(*P*, A_{Re})-**14CI**² enantiomers, τ_{phos} was around 450 μs . A similar trend was found for the quantum yields, with the **14CI**¹ pair emitting more brightly (Φ_{Phos} 9%) than the **14CI**² one (Φ_{Phos} 6%). The iodo helicene-NHC-Re diastereoisomers **14I**¹ and **14I**² were found less phosphorescent due to efficient quenching with the solvent. Diastereoisomers (*P*, A_{Re})-**14I**²/**14CI**² and (*P*, C_{Re})-**14I**¹/**14CI**¹ displayed similar CPL spectra (Figure 4e) with respective g_{lum} values of around $+5.3 \times 10^{-3}$ and $+5.6 \times 10^{-3}$ at 525 nm for the (*P*, A_{Re}) isomers, and (-4.4×10^{-4} and -1.4×10^{-3}) for the (*P*, C_{Re}) ones. Here again, a strong 'match / mismatch' effect was imposed by the helix and metal

stereochemistries. The manipulation of the Re^I stereochemistry thus enabled efficient optimization of the CPL response. Similar results were obtained for the azahelicene-NHC-rhenium complexes **16I**^{1,2,15}

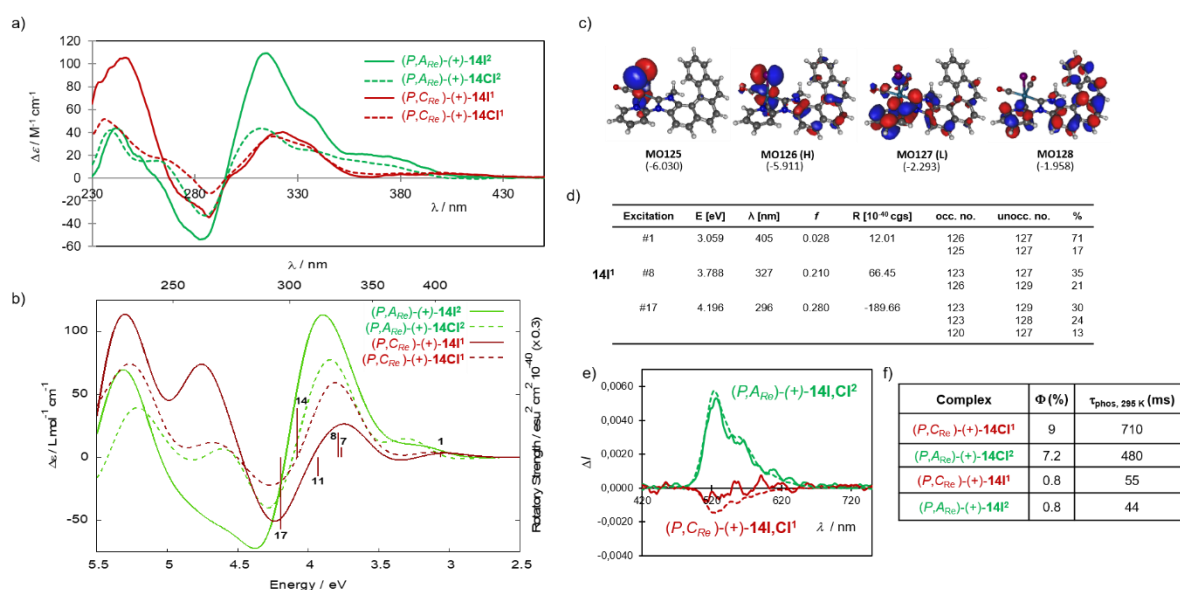


Figure 4. a) Experimental ECD spectra (CH₂Cl₂) of enantiomerically and diastereomerically pure Re^I complexes **14I**^{1,2} and **14CI**^{1,2} with *P* helices. b) Calculated ECD spectra of **14I**^{1,2} and **14CI**^{1,2} with selected transitions for **14I**¹ indicated as ‘stick spectra’. c) Selected MOs involved in the electronic transition of complex **14I**¹. d) Selected electronic transitions exhibiting strong rotational strengths. e) CPL spectra and f) phosphorescence quantum yields and lifetime of **14I**^{1,2} and **14CI**^{1,2} with *P* helices measured in deaerated CH₂Cl₂ solutions.

2.4. Photophysics and chiroptics of helicene-NHC complexes with non stereogenic metal centers (Pt, Cu, Au)

The photophysical and chiroptical properties of complexes **12a,b** were studied in deoxygenated solutions, both at room temperature and at 77 K, and in poly(methyl methacrylate) (PMMA) films.¹⁴ We found that the helicene ligand actually imparts significant rigidity and steric protection to these complexes, enabling them to emit in solution, a marked difference from their non-helicene counterparts.²⁰ Furthermore, the phosphorescence changed from unresolved to well-structured from room to low temperature, and the CPL activity was enhanced, from g_{lum} values of 5×10^{-3} (**12a**) and 2×10^{-3} (**12b**) in deaerated toluene at rt to 1.3×10^{-2} (**12a**) and 6.2×10^{-3} (**12b**) in a frozen matrix at 77 K (see Figure 5a for **12a**). We observed that multiple excited states contributed to optical transitions at rt while at lower temperature, the dissymmetry factor was consistent with single chiral excited state, which may explain its amplification. In 2 wt% doped PMMA films, the PLQY for **12a** and **12b** was improved by over six-fold and two-fold, respectively, thanks to restriction of the non-radiative processes, and the CPL g_{lum} value of around 10^{-3} was found for **12a**.

Finally, copper(II) complex **18**¹⁶ and gold(I) complex **20**¹³ displayed photophysical and chiroptical properties that were very close to their parent pro-ligand. This is explained by the

monodentate nature of the Hel-NHC ligand which interacts less efficiently with the metal in these closed-shell systems. Nevertheless, CP-phosphorescence was found for **18** and **20**, with g_{lum} values around 10^{-3} in solution.

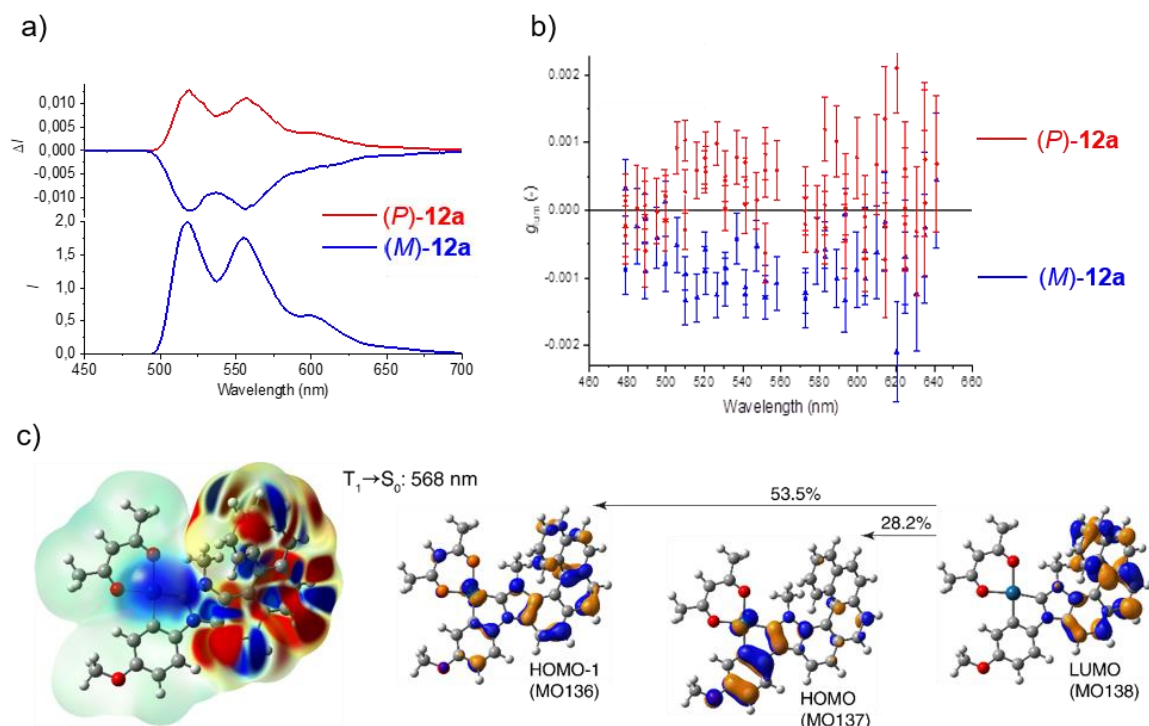


Figure 5. a) Experimental luminescence and CPL spectra of (*P*)- and (*M*)-**12a** in degassed 2-MeTHF at 77 K ($\lambda_{\text{ex}} = 365$ nm. b) Plot of g_{lum} values with emission wavelength obtained for 2 wt% PMMA film of **12a** enantiomers; $\lambda_{\text{ex}} = 313$ nm. c) Left: calculated electron density differences between the S_0 ground state and T_1 excited state, $\Delta\rho = \rho_l - \rho_e$, color-mapped on ρ_g for **12a**. Electron density moves from the red region to the blue region when moving from the excited state to the ground state. Right: The corresponding computed $T_1 \rightarrow S_0$ phosphorescence wavelengths along with dominant MO-pair contributions to emission transition.

Conclusions and outlook

The combination of classical coordination chemistry with uncommon helically shaped NHC ligands has revealed a powerful strategy to generate novel chiral organometallic architectures from either *N*-substituted or fused helicene-based imidazolium salts. Their topology and stereochemical structures could be finely analyzed by several techniques, including X-ray diffraction analysis. Importantly, being neutral and stable species, almost all complexes were readily obtained in diastereomerically and enantiomerically pure forms *via* HPLC over chiral stationary phases. This not only enabled us to generate pure compounds, but also to examine in details their structure-properties relationships, especially their photophysical and chiroptical

responses that were interpreted with the help of theoretical calculations. Overall, these new diversifications in organometallic helicene chemistry provided the molecules with unprecedented features and opened a new field. Ir- and Re-NHC-helicene complexes displayed very long-lived CPL-blue-green phosphorescence which may lead to future applications such as chiral dopants in CP-OLEDs, singlet oxygen sensitizers and selective photo-oxidizing agents for biological materials, or asymmetric photocatalysts or stereoselective quenchers.

It is also important to emphasize that the chirally helical transition metal complexes synthesized in our group are very good models for the development and evaluation of highly advanced theoretical methods, further confirming the main features found in our studies such as the presence of long-lived excited triplet states, providing additional insights such as contribution of spin-vibronic couplings.²¹ Further experimental studies such as transient EPR and transient absorption and emission spectroscopies will be future tools to better understand the dynamics and kinetics of the different excited states involved in the photophysics.

Novel chiral materials still need to be developed. Of special current focus are nanoparticles grafted with chiral monodentate or multidentate NHCs,^{8a,e,22} and incorporating helical chirality may be of interest to generate improved chiroptical responses, especially in less common domains such the near infrared, to discover novel properties such as chiral-induced spin selectivity (CISS effect) or novel photocatalytic and electrocatalytic reactivities. The link with biological activity is also an obvious interest due to the homochiral nature of living systems. Finally, there are still many original architectures to discover by implementing helical chirality into abnormal NHCs.²³

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Notes

[§] All $\Delta\epsilon$ values in this work are given in units of $\text{M}^{-1} \text{cm}^{-1}$, all molar rotations in degree $\text{cm}^2 \text{dmol}^{-1}$.

Biographical Information

Debsouri Kundu earned his Integrated BS-MS degree in Chemical Sciences from Indian Institute of Science Education and Research, Kolkata, in 2016. He subsequently obtained his Master of Science degree from Department of Physical Sciences at University of Chicago in 2017. Most recently, in 2024, he completed his Ph.D. as a Fellow of Marie Curie International Training Network (ITN HEL4CHIROLED) under the mentorship of Dr. Jeanne Crassous. His research interests include design and development of innovative organic materials and coordination complexes for organic electronics and medicinal chemistry.

Natalia del Rio received her PhD at the University of Paul Sabatier III (Toulouse, France) working on the synthesis of stable heterocyclic amino(phosphanylidene-s4-phosphorane) germylenes under the supervision of Dr. Tsuyoshi Kato. After her PhD, she moved as post-doctoral researcher to Sorbonne University to work with Louis Fensterbank and Matthieu Sollogoub groups on the synthesis and catalytic activity of β -cyclodextrin-NHC-gold(I) complexes. After a period at the IFPEN company, she worked as postdoctoral researcher at the Institut des Sciences Chimiques de Rennes, under the supervision of Dr. Jeanne Crassous, on helicene-based transition metal complexes with CPL activity and acted as Project Manager of the HEL4CHIROLED European ITN project.

Jeanne Crassous is a CNRS Research Director at the 'Institut des Sciences Chimiques de Rennes' (ISCR, Rennes, France). She received her PhD in 1996 from the Ecole Normale Supérieure de Lyon (ENS Lyon) on 'The Absolute Configuration of Bromochlorofluoromethane (CHFCIBr)' under the supervision of Prof. André Collet. After a one-year postdoctoral position on 'The Chirality of Fullerenes' in Prof. François Diederich's group (ETH Zurich, Switzerland), she was appointed CNRS researcher at the ENS Lyon in 1998 and then she joined the ISCR in 2005. She is currently coordinating a French national network (GDR CHIRAFUN, Chirality and multifunctionality) and coordinated the HEL4CHIROLED European ITN Project. In 2020, she received the National Prize of the Organic Chemistry Division of the French Chemical Society (DCO-SCF). In 2023, she was awarded the CNRS Silver Medal. She is also a Member of the European Academy of Science (EurASc), Chemistry Europe Fellow and Distinguished Member of the French Chemical Society. She is dealing with many fields of chirality (heteroatomic and organometallic helicenes, chiral π -conjugated systems and assemblies, fundamental aspects of chirality). She is studying chiroptics (electronic and vibrational circular dichroism, circularly polarized luminescence) for potential applications in optoelectronics and spintronics.

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