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Enantio-enriched CPL-active helicene-bipyridine-rhenium complexes

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The incorporation of a rhenium atom within an extended helical π-conjugated bi-pyridine system impacts the chiroptical and photophysical properties of the resulting neutral or cationic complexes, leading to the first examples of rhenium-based phosphors that exhibit circularly polarized luminescence.

2,2'-Bipyridine (bipy) derivatives are widely used N,N'-bidentate ligands in coordination chemistry, giving access to a great variety of complexes. The luminescence properties of dπ transition metal polypyridyl complexes have been increasingly studied for the development of new metal-based luminescent materials and sensing probes. Among them, [Re(N,N')(CO)₂X] complexes (X = halide, pyridyl (py) or isocyanide (CNR)) exhibit room-temperature (RT) phosphorescence from triplet metal-to-ligand (MLT) and/or intraligand charge-transfer (ILCT) states.

Such dπ-complexes find applications as electroswitchable emissive systems, cellular imaging agents, chirochromophores for photoredox chemistry, etc. It would therefore be of great interest to develop chiral analogues in order to benefit from the chiral version of emission, namely circularly polarized luminescence (CPL) which may potentially be used in cryptography or for 3D-displays.

In this communication, we describe the synthesis of tricarbonyl Re complex of general formula [Re(N,N')(CO)₂X] (X = halide, pyridyl or isocyanide) with N,N' being either achiral 3-(2-pyridyl)-4-aza[4]-helicene (1a) or chiral 3-(2-pyridyl)-4-aza[6]-helicene (M- and P-1b) (Scheme 1). The stereochemical features of these novel dπ-complexes are presented in detail. The chiroptical properties of enanto-enriched samples and the non-polarized and circularly polarized phosphorescence were measured experimentally and analyzed using quantum-chemical calculations.

Re³ complex 2a was obtained in 85% yield as a yellow-orange precipitate upon refluxing a solution of 1a and Re(CO)₂Cl in toluene for 5 hours (Scheme 1). It was fully characterized by multinuclear NMR spectroscopy (one set of peaks), by elemental analysis, UV-vis and emission spectroscopies. As compared to ligand 1a, the ¹H NMR spectrum of 2a shows strongly deshielded signals (except for H¹, H¹² and H¹³) with Δδ up to +0.8 ppm for H² (see Supporting Information, SI). The UV-vis spectrum of ligand 1a in CH₂Cl₂ displays a strong band at 295 nm (ε > 50 x 10⁴ M⁻¹ cm⁻¹), accompanied by several structured bands of lower intensity between 300 and 400 nm. Meanwhile, complex 2a shows several absorption bands between 230 and 370 nm (ε ~ 30-43 x 10³ M⁻¹ cm⁻¹) that can be assigned to intraligand π-π* transitions and a broad, low-energy absorption band between 370 and 480 nm (λ_max = 398 nm, ε = 12700 M⁻¹ cm⁻¹) related to the incorporation of the Re⁳ metal and predominantly assigned as ILCT with small contributions of MLCT character (vide infra). The absorption maximum at 398 nm appears red-shifted compared to the corresponding band in Re(2,2'-bpy)(CO)₂Cl [35 (350 nm) indicating extended π-conjugation.

Re³ complex 2a is red-phosphorescent in CH₂Cl₂ at RT (λ_max_phos = 678 nm, ϕ = 0.11%, τ = 25 ns, see SI). The phosphorescence originates from the triplet charge-transfer state. It is facilitated by spin-orbit coupling at the rhenium heavy atom and bathochromically shifted compared to that of Re(2,2'-bpy)(CO)₂Cl (λ_max_phos = 610 nm). At 77 K, the phosphorescence of 2a is significantly shifted to shorter wavelengths (λ_max_phos = 550 nm, τ = 7.9 μs). Such a hypsochromic shift is usually explained by inversion in energies of ²π-π* and ³MLCT triplet states and/or by rigidification of the system. Note that as usual in this class of complexes, the quantum yield at RT is rather low. In comparison, charged complexes of formula [Re(N,N')(CO)p]⁺ or [Re(N,N')(CO)₂CNR]⁻ typically display superior luminescence efficiency due to a stronger ligand field. For this reason, complexes 3a and 4a were prepared in good yields from 1a, according to Scheme 1. They were fully characterized by multinuclear NMR spectroscopy, elemental analysis, UV-vis spectroscopy, emission and X-ray crystallography. The 3a and 4a compounds crystallize in Fdd2 and P2₁/n centrosymmetric space groups respectively (Scheme 1). At this stage, it is worth noting that complexes 2a-4a are chiral at the rhenium centre, since the
Re atoms adopt a slightly distorted octahedral geometry, with three carbonyl groups being fac-oriented around the Re\(^{3+}\), as

classically seen in such rhenium(I) tricarbonyl diimine complexes.\(^3\) The equatorial planes are defined by the chelate

bipyridine ligand and two trans carboxyls. A third carboxyl and either the chlorine, the isocyanide or the pyridine are placed in

the apical positions. Note that in structures 3a, 4a the [6]helicene-bpy ligand exhibits a helicity angle (defined as angle between the
terminal rings of the helicene moiety) of \(\sim 35^\circ\) and the cyano

and pyridine ligand are directed towards it, thus defining the

\((P,A)^{Rb}_2\) and \((M,C)^{Rb}_2\) stereochemistry.\(^10\) However, in solution, the

helicene is not configurationally stable, and the Re center readily epimerizes \((vide infra)\). As expected, the charged complexes
displayed improved photophysical properties with similar UV-

visible and emission spectra as for 2a (see SI), but with higher

quantum yields (3a: 16%; 4a: 8.3%). These results prompted us to prepare tricarboxylrhenium(I) complexes bearing a


Racemic 1b was reacted with Re\((CO)_3\)Cl in refluxing toluene

for 5 hours, yielding after purification by chromatography two distinct diastereomeric Re(I) complexes (2b\(^1\) and 2b\(^2\), with 28% and 52% yields, respectively) as
evidenced by \(^1\)H and \(^{13}\)C NMR spectroscopy (for example \(^1\)H: 6.7 ppm for 2b\(^1\) and 6.9 ppm for 2b\(^2\), see SI).

Complex 2b\(^2\) crystallizes in a centrosymmetric space group \((P2_1/c)\) in which

two enantiomeric structures, namely \((M,C)^{Rb}_2\) and \((P,A)^{Rb}_2\)-2b\(^2\) are present (Scheme 1).\(^10\)

Note that a substantial distortion results from the bite angles between the chelating N atoms of the

helicene ligand, the rhenium centre and the chloride ligand

ranging between 82.6 and 84.3\(^\circ\). In complex 2b\(^2\) the chloride

atom is directed towards the helicene moiety, whereas it directs

outwards from the helicene core in the enantiomeric complexes

\((M,A)^{Rb}_2\) and \((P,C)^{Rb}_2\)-2b\(^1\). The helicity of the az[a]helicene moiety ranges between 47.0-66.2\(^\circ\), which is typical for

az[a]helicene derivatives (58\(^\circ\) for carbo[6]helicene).\(^8\) Finally,

complexation with Re affords an extended \(\pi\)-conjugation over the

whole molecule, as evidenced by the small NCCN dihedral angles between the two chelating pyridine moieties (-3.1,6-0.0\(^\circ\)).

The extended \(\pi\)-conjugation and the metal-ligand interaction are
evidenced by UV-visible spectroscopy since 2b\(^2,12\) display similar

UV-visible spectra with a set of several bands between 330 and 450

nm (\(\varepsilon \sim 7.25 \times 10^3\) M\(^{-1}\) cm\(^{-1}\)) that are bathochromically shifted and more intense compared to ligand 1b, together with a very

weak band observed between 450 and 500 nm (see Figure S21).

Calculations at the BHLYP/SV(P) level with the continuum solvent model for CH\(_2\)Cl\(_2\) reproduce well these data and show

that the low-energy band of the spectrum is dominated by an

ILCT transition, \(\pi(helicene) \rightarrow \pi^*(N=N)\), while the medium-energy bands are mostly \(\pi\)-to-\(\pi^*\) CT-like transitions localized

within the helicene moiety \((vide infra, SI)\) in agreement with

assignments of absorption spectra of related rhenium(I) systems, in particular for complexes with large \(\pi\)-conjugated ligands.\(^3,c\)

The overall contribution of the Re orbitals is low, meaning that the primary effect of the metal is to rigidify the system and

induce strong charge-transfer from the helical \(\pi\)-system to the

bipy N=N part of the ligand. The simulated spectral shapes and

band positions agree well with experiment. It is possible, though,

that the overall involvement of Re orbitals in the absorption

transitions is somewhat underestimated by the BHLYP functional

\(\phi\) \((vide infra)\). Re\(^{3+}\) complexes 2b\(^1,2\) are red-phosphorescent emitters in

CH\(_2\)Cl\(_2\) at RT (2b\(^1\): \(\lambda_{\text{max}}\text{phos} = 680\) nm, \(\phi = 0.13\%\), \(\tau = 27\) ns; 2b\(^2\): \(\lambda_{\text{max}}\text{phos} = 673\) nm, \(\phi = 0.16\%\), \(\tau = 33\) ns; for details see SI).

At 77 K, these complexes display phosphorescence at shorter

wavelengths (2b\(^1\): \(\lambda_{\text{max}}\text{phos} = 560\) nm, \(\tau = 46\) μs; 2b\(^2\): \(\lambda_{\text{max}}\text{phos} =

554 nm, \(\tau = 43\) μs \((vide supra)\). Note that the emission properties of
diastereomers 2b\(^1,2\) are only slightly different and (for \(\tau\) and \(\phi\)) within the uncertainty in the measurements (see SI).

Enantiopure complexes \((M,A)^{Rb}_2\)-2b\(^1\) and \((M,C)^{Rb}_2\)-2b\(^2\) were then

prepared from enantiopure M-1b (their mirror-images \((P,A)^{Rb}_2\)-2b\(^1\)

and \((P,C)^{Rb}_2\)-2b\(^2\) from P-1b). Enantiopure complexes 2b\(^1,2\)

display similar molar rotation (MR) values to 1b in CH\(_2\)Cl\(_2\):

\((P,C)^{Rb}_2\)-(+)2b\(^1\): \(P = +9260\) degree cm\(^2\) dmol\(^{-1}\) (±5%), calc.

BHLYP +12721; \((P,A)^{Rb}_2\)-(+)2b\(^2\): \(P = +10260\) (±5%), calc.

BHLYP +11888 degree cm\(^2\) dmol\(^{-1}\); \((P,-1)^{Rb}_2\): \(P = +12000\)

(±5%), calc. BHLYP +14176, see SI). The ECD spectrum of P-

2b\(^1\) shows a strong negative band around 261 nm \((\Delta\epsilon = -114\) M\(^{-1}\)

\(\text{cm}^2\)) and strong positive ones at 350 (+81 M\(^{-1}\) cm\(^2\)) and 368 nm

(+76 M\(^{-1}\) cm\(^2\)) accompanied by weaker bands between 380 and 450 nm (20-40 M\(^{-1}\) cm\(^2\)) and an even weaker one around 480 nm

but of opposite sign \((\Delta\epsilon \sim -0.6\) M\(^{-1}\) cm\(^2\)). Diastereomeric complex \((P,A)^{Rb}_2\)-(+)2b\(^2\) exhibits the same ECD active bands as

2b\(^1\) but they are more intense. A comparison with experimental

ECD of 1a enantiomers is displayed in Figure 1. The calculated

(BHLYP/SV(P) with the continuum solvent model for CH\(_2\)Cl\(_2\))

spectra of 2b\(^1,2\) qualitatively agree well with the experimental

results (Figure 3 and S5). A detailed analysis of dominant excitations in the low- and medium-energy parts of the simulated

spectra of 2b\(^1,2\) indicates that the low-energy tail of the first

positive ECD band is caused by excitation no. 1 calculated at \(E =

3.3\) eV (375 nm). The excitation can be assigned as a \(\pi-\pi^*\) ILCT transition involving the helicene-centered HOMO (H), H-1, and

the bipyridine N=N-centered LUMO (L), for example for 2b\(^1\): H-

L 51% and H-1-L 18% (see Figure 3 and SI). The second dominant 2b\(^1\) excitation is no. 5 calculated at \(E = 3.8\) eV (330

nm) with the strongest rotatory strength. It involves two main contributions from \(\pi\) and \(\pi^*\) orbital pairs localized mostly in the

helicene moiety: H-L+1 and H-1-L+1 (respectively 43% and 25% for 2b\(^1\)). The excitation reveals partial CT character.

A novel aspect of these rhenium(I) helicene-based complexes

is that they are CPL active (Figure 2, top panels).\(^7,8\) To the best of our

knowledge, these are the first examples of CPL-active phosphorescent rhenium complexes. Indeed phosphorescent

\((P,A)^{Rb}_2\) and \((M,C)^{Rb}_2\)-2b\(^2\) enantiomers displayed mirror-imaged

CPL spectra (Figure 2) with opposite \(\Theta\) values \((\Theta_{(P,A)^{Rb}_2}\text{-}2b^2): +3.1 \times 10^3; \Theta_{(M,C)^{Rb}_2}\text{-}2b^2: -2.8 \times 10^3\) around the emission

maximum (-670 nm). These values are of the same order as for the

1b ligand enantiomers \((\Theta_{(S)} \pm 10^3)\) but lower than those of

previously published platinal[6]helicenes \((\Theta_{(S)} \sim \pm 10^3)\),\(^3\) because Re orbitals are less involved in the helical \(\pi\)-system of the

11 molecule \((vide supra)\).
In order to improve the efficiency of the chiroptical and photophysical properties, tricarbonyl-isocyanide-helencene-bipy-Re$^3$ complex M-3b was prepared (see Scheme 1) in 75% yield from either ($MA^Re$)(-)2$^b$ or ($MC^Re$)(-)2$^b$. In this complex, the Re center appeared labile and 3b was obtained as a mixture of ($MA^Re$)-3$^b$ and ($MC^Re$)-3$^b$ as observed by $^1$H and $^1$C NMR spectroscopy (diastereomeric ratio 50:50, see Figure S27) regardless of the diastereomeric purity of the starting compound used (either 2$^b$ or 2$^b$. Nevertheless, as expected, this diastereomeric mixture displayed an improved quantum yield ($\lambda_{\text{max}}$ = 598 nm, $\phi = 6\%$, $\tau = 79$ μs; see SI) as compared to 2$^b$. The UV-vis spectrum of 3$^b$ displays the same shape as 2$^b$ (see Figure S21). Compared to ($PC^Re$)-2$^b$ and ($PA^Re$)-2$^b$, cationic diastereomeric mixture of Re$^3$ complexes P-3$^b$ displays an additional positive CD-active band around 450 nm ($\Delta\varepsilon = 17.5$ M$^{-1}$ cm$^{-1}$). As for 2$^b$, this latter band does not involve the Re center, but corresponds to the H-L transition (>74%) with strong charge transfer from the π-helicene to the bipy moiety, as evidenced by BHLYP calculations (see Figure 3 and SI). The appearance of the 450 nm band is caused mainly by a bathochromic shift of the first singlet excitation. This charge transfer excitation is likely responsible for the molar rotations as compared to 2$^b$. 

Finally, mirror-imaged CPL spectra were obtained in CH$_2$Cl$_2$ for ($MA^Re$)-3$^b$ and ($PA^Re$)-3$^b$ (Figure 2) with respective $\beta_{\text{sum}}$ values of -0.0015 and +0.0013. Overall, cationic Re$^3$ complexes display similar CPL characteristics as neutral ones, but combined with a higher quantum yield, the polarized emitted light is stronger. Although the Re d orbitals are not strongly involved in the electronic π systems of these novel metallo-helencenes, the metal helps to increase the π-conjugation pathway and promotes charge transfer excitations within the π-helical ligand. In addition, the presence of the rhenium heavy atom makes these complexes chiral phosphores with unprecedented CPL activity.

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Figure 3. Left: experimental CD spectra of enantiopure complexes $(P, C^N)$-$(+)\text{-}2b^2$ (light blue), $(P, C^A)$-$(+)\text{-}2b^3$ (dark blue) and of $(M, C^A)$-$(-)\text{-}3b^{2L}$ (dotted green) and $(P, C^A)$-$(+)\text{-}3b^{3L}$ (plain green). Right: calculated CD spectra of $(P, C^A)$-$(+)\text{-}2b^2$ and $(P, C^A)$-$(+)\text{-}2b^3$ and Boltzmann-averaged spectrum for $P$-$3b^{3L}$ conformers. No spectral shift has been applied. View of HOMO and LUMO of $2b^3$ and $3b^3$ [0.04 au]. First excitation energies indicated by dots on the abscissa.

Notes and references

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† Note that enantiopure (+) and (-) complexes (1a)Ret(OC)Br were prepared by chiral HPLC and they displayed very weak CD activity $(\Delta e = 20 \text{ M}^{-1} \text{cm}^{-1}$, see Figure S25).

† The direct comparison between experimental and calculated lifetimes must be treated with some caution, as the former are also affected by non-radiative decay pathways, which may be negligible even at 77 K. We assume that the non-radiative decay rates for the complexes are similar under these conditions.

