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 d6 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)X]X+ complexes (X = halide, pyridyl (py) or isocyanide (CNR)) exhibit room-temperature (RT) phosphorescence from triplet metal-to-ligand (ML) and/or intraligand charge-transfer (ILCT) states.

Such d6-complexes find applications as electroswitchable emissive systems, cellular imaging agents, chromophores 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 Re3 complexes of general formula [Re(NN')(CO)X]X+ (X = halide, pyridyl or isocyanide) with N,N'-being either achiral 3-(2-pyridyl)-4-azaj[4]-helicene (1a) or chiral 3-(2-pyridyl)-4-aza[6]-helicene (M- and P-1b) (Scheme 1). The stereochemical features of these novel d6-complexes are presented in detail. The chiroptical properties of enantio-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 1a8 and Re(CO)3Cl 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 H3, H12 and H13) with Δδ up to +0.8 ppm for H1 (see Supporting Information, SI). The UV-vis spectrum of ligand 1a in CH2Cl2 displays a strong band at 295 nm (ε > 50 x 103 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 (λmax = 398 nm, ε = 12700 M⁻¹ cm⁻¹) related to the incorporation of the Re3 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)3Cl (350 nm) indicating extended π-conjugation.

Re3 complex 2a is red-phosphorescent in CH2Cl2 at RT (λmax(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)3Cl (λmax(phos) = 610 nm). At 77 K, the phosphorescence of 2a is significantly shifted to shorter wavelengths (λmax(phos) = 550 nm, τ = 7.9 μs). Such a hypsochromic shift is usually explained by inversion in energies of 3π-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(NN')(CO)py]3+ or [Re(NN')(CO)CNR]3+ 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/c 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, as classically seen in such rhenium(I) tricarbonyl diimine complexes. The equatorial planes are defined by the chelate bipyridine ligand and two trans carbonyls. A third carbonyl and either the chlorine, the isocyanide or the pyridine are placed in the apical positions. Note that in structures 3a, 4a the [4]helicene-bpy ligand exhibits a helicity angle (defined as angle between the terminal rings of the helicene moiety) of ~35° and the cyanide and pyridine ligand are directed towards it, thus defining the (P,A(Re)) and (M,C(Re)) stereochemistry. 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 tricarbonylrhenium(I) complexes bearing a configurationally stable enantiopure [6]helicene-bipy ligand.

Racemic 1b was reacted with Re(CO)₅Cl in refluxing toluene for 5 hours, yielding after purification by chromatography two distinct diastereomeric Re(I) complexes (2bi and 2b2, with 28% and 52% yields, respectively) as evidenced by ¹H and ¹³C NMR spectroscopy (for example H13: 6.7 ppm for 2b1 and 6.9 ppm for 2b2, see SI). Complex 2b2 crystallizes in a centrosymmetric space group (P2₁/C) in which two enantiomeric structures, namely (M,C(Re)) and (P,A(Re)-2b) are present (Scheme 1). Note that a substantial distortion results from the bite angles between the chelating N atoms of the helicenic ligand, the rhenium centre and the chloride ligand ranging between 82.6 and 84.3°. In complex 2b1 the chlorine atom is directed towards the helicene moiety, whereas it directs outwards from the helicene core in the enantiomeric complexes (M,A(Re)) and (P,C(Re)-2b). The helicity of the azal[6]helicene moiety ranges between 47.0-66.2°, which is typical for azal[6]helicene derivatives (58° for carbo[6]helicene). Finally, complexation with Re affords an extended π-conjugation over the whole molecule, as evidenced by the small NCCN dihedral angles between the two chelating pyridine moieties (~3.1-6.0°). The extended π-conjugation and the metal-ligand interaction are evidenced by UV-vis spectroscopy since 2b1-2 display similar UV-vis spectra with a set of several bands between 330 and 450 nm (λ ~ 7.25 x 10⁴ M⁻¹ cm⁻¹) that are bathochromically shifted and more intense compared to ligand 1b1, together with a very weak band observed between 450 and 500 nm (see Figure S21).

Calculations at the B3LYP/SV(P) level with the continuum solvent model for CH₂Cl₂ reproduce well these data and show that the low-energy band of the spectrum is dominated by an ILCT transition, π(helicene) → π⁺(N=N), while the medium-energy bands are mostly π-π* '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 π-conjugated ligands. 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 π-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 B3LYP functional (vide infra). Re² complexes 2b1,2 are red-phosphorescent emitters in CH₂Cl₂ at RT (2b1: λmax phosph = 680 nm, φ = 0.13%, τ = 27 ns; 2b2: λmax phosph = 673 nm, φ = 0.16%, τ = 33 ns; for details see SI). At 77 K, these complexes display phosphorescence at shorter wavelengths (2b1: λmax phosph = 560 nm, τ = 46 µs; 2b2: λmax phosph = 554 nm, τ = 43 µs (vide supra). Note that the emission properties of diastereomers 2b1-2 are only slightly different and (for τ and φ) within the uncertainty in the measurements (see SI).

Enantiopure complexes ((M,A(Re))-2b1 and (M,C(Re))-2b2 were then prepared from enantiopure 1b (their mirror-images (P,A(Re))-2b1 and (P,C(Re))-2b2 from 1b). Enantiopure complexes 2b1,2 display similar molar rotation (MR) values to 1b in CH₂Cl₂: (P,C(Re))-(+)-2b1: [α]²ⁱ₀ = +9260 degree cm²/dmol (±5%), calc. B3LYP +12721; (P,A(Re))-(+)-2b²: [α]²⁴₀ = +10260 (±5%), calc. B3LYP +11888 degree cm²/dmol; P-(-)-1b: [α]²⁴₀ = +12000 (±5%), calc. B3LYP +14176, see SI). The ECD spectrum of 2b1 shows a negative band around 261 nm (Δε = -114 M⁻¹ cm⁻¹) and strong positive ones at 350 (+81 M⁻¹ cm⁻¹) and 368 nm (+76 M⁻¹ cm⁻¹) accompanied by weaker bands between 380 and 450 nm (20-40 M⁻¹ cm⁻¹) and an even weaker one around 480 nm but of opposite sign (Δε ~ -0.6 M⁻¹ cm⁻¹). Diastereomeric complex (P,A(Re))-(-)-2b² exhibits the same ECD active bands as 2b1 but they are more intense. A comparison with experimental ECD of 1a enantiomers is displayed in Figure 1. The calculated (B3LYP/SV(P) with the continuum solvent model for CH₂Cl₂) spectra of 2b1,2 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 2b1-2 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 π-π* ILCT transition involving the helicene-centered HOMO (H), H-1, and the bipyridine N=N-centered LUMO (L), for example for 2b1: H-H-L 51% and H-1-L 18% (see Figure 3 and SI). The second dominant 2b1 excitation is no. 5 calculated at E = 3.8 eV (330 nm) with the strongest rotatory strength. It involves two main contributions from π and π* orbital pairs localized mostly in the helicene moiety: H-L+1 and H-1-L+1 (respectively 43% and 25% for 2b1). 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). To the best of our knowledge, these are the first examples of CPL-active phosphorescent rhenium complexes. Indeed phosphorescent (P,A(Re))-2b1 and (M,C(Re))-2b² enantiomers displayed mirror-imaged CPL spectra (Figure 2) with opposite gsum values ((P,A(Re))-2b1: +3.1 x 10⁻³ and (M,C(Re))-2b²: -2.8 x 10⁻³) around the emission maximum (~670 nm). These values are of the same order as for the 1b ligand enantiomers (gsum ~±10⁻³) but lower than those of previously published platinal[6]helicenes (gsum ~±10⁻³), because Re orbitals are less involved in the helical π-system of the 110 molecule (vide supra).
In order to improve the efficiency of the chiraloptical and photophysical properties, tricarbonyl-isocyanide-helicene-bipy-Re$^\text{III}$ complex M-3b was prepared (see Scheme 1) in 75% yield from either (MAC)$_{\text{Re}}^\text{-}$(−)$\text{-}2\text{b}^1$ or (MAC)$_{\text{Re}}^\text{-}$(−)$\text{-}2\text{b}^2$. In this complex, the Re center appeared labile and 3b was obtained as a mixture of (MAC)$_{\text{Re}}^\text{-}$(−)$\text{-}3\text{b}^1$ and (MAC)$_{\text{Re}}^\text{-}$(−)$\text{-}3\text{b}^2$ 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 2b$_1$ or 2b$^2$ or 2b$_{1,2}$). Nevertheless, as expected, this diastereomeric mixture displayed an improved quantum yield ($\lambda_{\text{max}}$ $\text{phox} = 598$ nm, $\phi = 6\%$, $\tau = 79$ μs; see SI) as compared to 2b$_{1,2}$. The UV-vis spectrum of 3b$_{1,2}$ displays the same shape as 2b$_1$ (see Figure S21). Compared to (P,C)$_{\text{Re}}^\text{-}$(−)$\text{-}2\text{b}^1$ and (P,A)$_{\text{Re}}^\text{-}$(−)$\text{-}2\text{b}^2$, cationic diastereomeric mixture of Re$^\text{III}$ complexes P-3b$_{1,2}$ displays an additional positive CD-active band around 450 nm ($\Delta\epsilon = 17.5$ M$^{-1}$ cm$^{-1}$). As for 2b$_{1,2}$, this latter band does not involve the Re center, but corresponds to the H-L transition (>74%) with strong charge transfer from the π-heliciene 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 enhancement of molar rotations as compared to 2b$_{1,2}$ (Figure 2) with respective $\gamma$ values of -0.0015 and +0.0013. Overall, cationic Re$^\text{III}$ 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-helicenes, 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 phosphors with unprecedented CPL activity.

Finally, mirror-imaged CPL spectra were obtained in CH$_2$Cl$_2$ for (MAC)$_{\text{Re}}^\text{-}$(−)$\text{-}3\text{b}^1,2$ and (P,A)$_{\text{Re}}^\text{-}$(−)$\text{-}3\text{b}^1,2$ (Figure 2) with respective $\gamma$ values of -0.0015 and +0.0013. Overall, cationic Re$^\text{III}$ 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-helicenes, 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 phosphors with unprecedented CPL activity.

In conclusion, the first CPL-active rhenium complexes have been prepared by coordination of enantiopure [6]helicene-bipyridine type ligands. Their chiroptical and photophysical properties (optical rotation, electronic circular dichroism, non-polarized and circularly polarized luminescence, quantum yields, phosphorescence lifetimes) have been studied and analyzed with the help of quantum-chemical calculations.

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Notes and references

See for example:


Chiral and emissive rhenium complexes are still very rare, see for example:


Enantiopure "chiral at rhenium" complexes are still very rare. Selected examples:


For the stereochemical descriptors see SI and A. von Zelewsky, Stereochemistry of Coordination Compounds, J. Wiley & Sons, Chichester, 1996.