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]0/+ 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 electrowritable emissive systems,1a cellular imaging agents,1b,2d 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.3b,c,d

In this communication, we describe the synthesis of tricarbonyl Re3 complexes of general formula [Re(N,N')(CO)X]0/+ (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 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 1a and Re(CO)5Cl 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 H2, H12 and H14) with ∆δ up to +0.8 ppm for H5 (see ESI†). The UV-vis spectrum of ligand 1a in CH2Cl2 displays a strong band at 295 nm (ε > 50 × 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 × 104 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 = 12 700 M−1 cm−1)
related to the incorporation of the Re³ metal and predominantly assigned as ILCT with contributions of MLCT character (vide infra). The absorption maximum at 398 nm appears red-shifted compared to that of Re(2,2'-bpy)(CO)Cl³F (350 nm) indicating extended π-conjugation.

Re³ complex 2a is red-phosphorescent in CH₂Cl₂ at RT (τ° = 678 nm, 5% at 25 ns, see ESI†). The phosphorescence originates from the triplet charge-transfer state. It is facilitated by spin-orbit coupling at the ruthenium heavy atom and bathochromically shifted compared to that of Re(2,2'-bpy)(CO)Cl (τ° = 610 nm). At 77 K, the phosphorescence of 2a is significantly shifted to shorter wavelengths (τ° = 550 nm, τ = 7.9 μs). Such a hypsochromic shift is usually explained by inversion of the 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(N⁺N⁻)CO]³⁺ or [Re(N⁺N⁻)CO]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/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 Re³, 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 4π-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 (PA⁵) and (MC⁶) 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 ESI†), 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-bpy ligand.

Racemic 1b was reacted with Re(CO)³Cl in refluxing toluene for 5 hours, yielding after purification by column chromatography two diastereomeric Re(i) complexes (2b and 2b', with 28% and 52% yields, respectively) as evidenced by ¹H and ¹³C NMR spectroscopy (for example H¹²: 6.77 ppm for 2b and 6.99 ppm for 2b', see ESI†). Complex 2b⁵ crystallizes in a centrosymmetric space group (P2₁/n(C)) in which two enantiomeric structures, namely (MC⁶) and (PA⁵)-2b are present (Scheme 1). 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°. In complex 2b the chlorine atom is directed towards the helicene moiety, whereas it directs outwards from the helicene core in the enantiomeric complexes (MA⁵) and (P,CA⁵)-2b⁴. The helicity of the az[6]helicene moiety ranges between 47.0–66.2°, which is typical for az[6]helicene derivatives (58° for carbox[6]helicene). Complex 2b shows similar UV-visible and emission spectra as for 2a, with a slightly red-shifted absorption maximum at 398 nm, as expected (vide infra). The extended π-conjugation of 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 2b shows similar UV-vis spectra with a set of several bands between 330 and 450 nm (ε ~ 7–25 × 10³ 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 Fig. S21, ESI†). Calculations at the BHHLYP/SVP level with a 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(ex) → π*(N=N)). The medium-energy bands are mostly π-π* “CT-like” transitions localized within the helicene moiety (vide infra, ESI†) in agreement with assignments of absorption spectra of related rhenium(i) compounds, 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 BHHLYP functional (vide infra). Re² complexes 2b and 2a are red-phosphorescent emitters in CH₂Cl₂ at RT (τ° = 680 nm, φ = 0.13%, τ = 27 ns; 2b: τ° = 673 nm, φ = 0.16%, τ = 33 ns; for details see ESI†). At 77 K, these complexes display phosphorescence at shorter wavelengths (2b: τ° = 560 nm, τ = 46 μs; 2b: τ° = 554 nm, τ = 43 μs (vide supra). Note that the emission properties of diastereomers 2b and 2b' are only slightly different and (for τ and φ) within the uncertainty in the measurements (see ESI†).
the helicene-centered HOMO (H), \(-1\), and the bipyridine \(N^+N^-\)-centered LUMO (L), for example for \(2b^1\): \(H-L\) 51\% and \(H-1-L\) 18\% (see Fig. 3 and ESIF). The next dominant \(2b^1,2\) excitation is no. 5 calculated at \(E = 3.8\ E\)V (330 nm) with the strongest rotary 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(II) helicene-based complexes is that they are CPL active (Fig. 2, top panels).\(^7\) To the best of our knowledge, these are the first examples of CPL-active phosphorescent rhenium complexes. Indeed phosphorescent \((P,A)^{Re}\) and \((M,C)^{Re}\) \(2b^2\) enantiomers displayed mirror-imaged CPL spectra (Fig. 2) with opposite \(g_{\text{sum}}\) values \((|P,A|^ {Re})\ 2b^2: +3.1 \times 10^{-3}\) and \((M,C)^{Re}\) \(2b^2: -2.8 \times 10^{-3}\) around the emission maximum (~670 nm). These values are of the same order as for the \(1b\) ligand enantiomers \((g_{\text{sum}} \sim \pm 10^{-3})\) but lower than those of previously published planar helicenes \((g_{\text{sum}} \sim \pm 10^{-3})\)\(^6\) because 

In order to improve the efficiency of the chiroptical and photophysical properties, tricarbonyl-isocyanide-helicene-bipy-ReI complex \(M-3b\) was prepared (see Scheme 1) in 75\% yield from either \((M,A)^{Re}\) \(-2b^1\) or \((M,C)^{Re}\) \(-2b^2\). In this complex, the Re center appeared labile and \(3b\) was obtained as a mixture of \((M,A)^{Re}\) \(3b^1\) and \((M,C)^{Re}\) \(3b^2\) as observed by \(^1\)H and \(^1\)C NMR spectroscopy (diastereomeric ratio 50:50; see Fig. S27, ESIF) 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 exhibited an improved quantum yield (\(\phi_{\text{max}} = 598\ nm, \phi = 6\%\), \(\tau = 79\ ms\); see ESIF) as compared to \(2b^1,2\). The UV-vis spectrum of \(3b^1,2\) displays the same shape as \(2b^1\) (see Fig. S21, ESIF). Compared to \((P,A)^{Re}\) \(2b^1\) and \((P,A)^{Re}\) \(2b^2\), cationic diastereomeric mixture of ReI complexes \(P-3b^1,2\) demonstrates an additional positive CD-active band around 450 nm \((\Delta\varepsilon = 17.5\ M^{-1}\ \text{cm}^{-1})\). 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 \(\pi\)-helicene to the bipy moiety, as evidenced by BLYP calculations (see Fig. 3 and ESIF). 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 \(2b^1,2\) \((\phi_{\text{sum}})^{Re}\) \(3b^1: \phi^1 = 15\ 040\ \text{deg cm}^2\ \text{dmol}^{-1} (\pm 5\%); (C = 8.8 \times 10^{-5}\ M, \text{CH}_2\text{Cl}_2); (M,C)^{Re}: (\phi_{\text{sum}})^{-} = -14\ 230 (\pm 5\%); (C = 9.7 \times 10^{-5}\ M, \text{CH}_2\text{Cl}_2); \text{calc. BLYP Boltzmann average for}\ 3b^1,2\ \text{conformers is} +14\ 034\ \text{deg cm}^2\ \text{dmol}^{-1}\text{ for the P-isomers, see ESIF).}

Quantum-chemical calculations of luminescence properties have been performed for \(2b^1,2\) and \(3b^1,2\). The results support the experimental assignments: The energies of \(T_1 \rightarrow S_0\) phosphorescence transitions (<2.1 eV) are similar for both \(2b^1,2\) and \(3b^1,2\) and agree fairly well with the experimental data (Table S5, ESIF). An overestimation of the calculated versus measured energies is consistent with a blue-shift of calculated \(2b^1,2\) and \(3b^1,2\) absorption and CD spectra. The emission energies from spin-orbit (SO) calculations agree with non-SO calculations but the former allow predictions of the phosphorescence lifetimes. Application of the BLYP functional along with the Tamm-Dancoff approximation (see ESIF) resulted in much too high emission lifetimes (Table S6, ESIF). As the involvement of Re orbitals facilitates the formally spin-forbidden \(T_1 \rightarrow S_0\) phosphorescence transitions via spin-orbit coupling, decreasing the corresponding lifetimes, too high \(\tau\) calculated with BLYP may indicate that the metal orbital contributions

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**Fig. 1** Experimental CD spectra of enantiopure \(M-(-)-(\text{dotted red})\) and \((P, (+)-1b\) (plain red) and enantiopure ReI complexes \((M,A)^{Re}\) \(-2b^1\) and \((P,C)^{Re}\) \(-2b^2\) (light blue) and \((M,C)^{Re}\) \(-2b^2\) and \((P,A)^{Re}\) \(-2b^2\) (dark blue). Inset: CD spectra of \(-\) and \((+)\) \(2b^1\) between 450–550 nm.

**Fig. 2** CPL (upper curves within each panel) and total luminescence (lower curves within each panel) spectra of \(M-(-)-(+1b\) (left red), \((P, (+)-1b\) (left black), \(M-(-)-2b^2\) (middle red), \((P, (+)-2b^2\) (middle black), \(M-(-)-3b^1,2\) (right red), \((P, (+)-3b^1,2\) (right black) in degassed CH2Cl2 solution (1 mM) at 295 K, upon excitation at 400, 456–461, and 458–468 nm, respectively.

**Fig. 3** Left: experimental CD spectra of enantiopure complexes \((P,C)^{Re}\), \((+)-2b^2\) (light blue), \((P,A)^{Re}\) \((-)-(+)\) \(2b^2\) (dark blue) and of \((M,C)^{Re}\) \(-3b^1,2\) (dotted green) and \((P,C)^{Re}\) \(-3b^1,2\) (plain red). Right: calculated CD spectra of \((P,C)^{Re}\) \(2b^1\) and \((P,A)^{Re}\) \(2b^2\) and Boltzmann-averaged spectrum for \(P-3b^1,2\) conformers. No spectral shifts were applied. View of HOMO and LUMO of \(2b^1\) and \(2b^2\) (0.04 au). First excitation energies indicated by dots on the abscissa.
to the frontier MOs are somewhat too small. The performance of a given functional for singlet vs. triplet transitions is not necessarily the same. When applying a computational protocol for emission lifetimes devised recently by Mori et al.\textsuperscript{11} for organometallic complexes (full TDDFT with the B3LYP functional), a dramatic improvement of the lifetimes and some lowering of the emission energies (to ~1.9 eV) was obtained (Table S7, ESI\textsuperscript{[†]}), which correlates with increased participation of Re orbitals in the frontier MOs at the triplet geometries. Notably the experimental trend of an increase in emission lifetime by roughly an order of magnitude when going from 2b\textsubscript{1,2} to 3b\textsubscript{1,2} is correctly reproduced with B3LYP and qualitatively consistent with lesser metal orbital participation (lesser MLCT character) in the \(T_1\) emission transitions for 3b\textsubscript{1,2} as compared to 2b\textsubscript{1,2} (see ESI\textsuperscript{[†]}).\textsuperscript{8,ao,b}

Finally, mirror-imaged CPL spectra were obtained in CH\textsubscript{2}Cl\textsubscript{2} for (\textit{MeA}C\textsubscript{6}H\textsubscript{5})\textsubscript{3}Br and (\textit{PhA}C\textsubscript{6}H\textsubscript{5})\textsubscript{3}Br (Fig. 2) with respective \(\gamma_{\text{ESR}}\) values of ~0.0015 and +0.0013. Overall, cationic Re\textsuperscript{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 \(\pi\)-systems of these novel metallo-helicenes, the metal helps to increase the \(\pi\)-conjugation pathway and promotes charge-transfer excitations within the \(\pi\)-helical ligand. In addition, the presence of the rhenium heavy atom makes these complexes chiral phosphors with unprecedented CPL activity.

We thank the Ministère de l’Education Nationale, de la Recherche et de la Technologie, the CNRS, the ANR (10-BLAN-724-1-NCPCH3 and 12-BS07-0004-METALHEL-01) and the LIA Rennes-Durham for financial support. J.A. acknowledges the UB Center for Computational Research and thanks the National Science Foundation (CHE 1265833) for financial support. M.S. thanks the Foundation for Polish Science Homing Plus program co-financed by the European Regional Development Fund and the Ministry of Science and Higher Education in Poland scholarship. G.M. thanks NIH MBRS (1 SC3 GM089589-05 and 3 S06 GM008192-27S1) and the Henry Dreyfus Teacher-Scholar Award for financial support.

Notes and references