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HAL Id: hal-01109443
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Submitted on 3 Mar 2015

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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 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)3X]4+/3+ complexes (X = halide, pyridyl (py) or isocyanide (CN)) 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, chiroptical properties 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 Re⁴ complexes of general formula [Re(N,N')(CO)3X]4+/3+ (X = halide, pyridyl or isocyanide) with N,N’-N’ being either achiral 3-(2-pyridyl)-4-azao[4]helicene (1a) or chiral 3-(2-pyridyl)-4-azao[6]helicene (M- and P-1b) (Scheme 1). The stereochemical features of these novel d6-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 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 H², H'¹² and H'¹⁰) with Δδ up to +0.8 ppm for H'₁⁰ (see Supporting Information, SI). The UV-vis spectrum of 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 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 = 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 phosphoryl = 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 phosphoryl = 610 nm). At 77 K, the phosphorescence of 2a is significantly shifted to shorter wavelengths (λmax phosphoryl = 550 nm, τ = 7.9 µs). Such a hypsochromic shift is usually explained by inversion in energies of π–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)₃py]⁺ or [Re(N,N')(CO)₃CN]⁻ 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 Fd3d 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, 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) and (M, C) stereochemistry. However, in solution, the helicene is not configurationally stable, and the Re center readily epimerizes (vide infra).

Confirmation of the Re coordination of the ligand was obtained from the NMR spectra of 1a (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 2b the chloride anion is directed towards the helicene moiety, whereas it directs outwards from the helicene core in the enantiomeric complexes (M, A) and (P, C)-2b. The helicity of the az[6]helicene moiety ranges between 47.0-66.2°, which is typical for az[6]helicene derivatives (58° for carb[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 (~3,16.0°). The extended π-conjugation and the metal-ligand interaction are evidenced by UV-vis spectroscopy since 2b display similar UV-vis spectra with a set of several bands between 330 and 450 nm (ε ~ 7-25 × 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 BLYP/SV(P) level with the continuum solvent model for CHCl3 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-to-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 BLYP functional (vide infra). Re^I complexes 2b are red-phosphorescent emitters in CHCl3 at RT (2b: λmax = 680 nm, φ = 0.13%, τ = 27 ns; 2b: λmax = 673 nm, φ = 0.16%, τ = 33 ns; for details see SI). At 77 K, these complexes display phosphorescence at shorter wavelengths (2b: λmax = 560 nm, τ = 46 μs; 2b: λmax = 554 nm, τ = 43 μs) (vide supra). Note that the emission properties of diastereomers 2b are only slightly different and (for τ and φ) within the uncertainty in the measurements (see SI).

Enantiopure complexes (M, A)-2b and (M, C)-2b were then prepared from enantiopure M-1b (their mirror-images (P, C)-2b and (P, A)-2b) from P-1b. Enantiopure complexes 2b display similar molar rotation (MR) values to 1b in CHCl3: (P, C)-(+)-2b: [θ]2b^2 = -5200 degree cm^2/dmol (±5 %), calc. BLYP +12721; (P, A)-(+)-2b: [θ]2b^2 = +10260 (±5 %), calc. BLYP +11888 degree cm^2/dmol; P-(+)-1b: [θ]2b^2 = +12000 (±5 %), calc. BLYP +14176, see SI). The ECD spectrum of P-2b 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. The diastereomeric complex (P, A)-(+)-2b exhibits the same ECD active bands as 2b but they are more intense. A comparison with experimental ECD of 1a enantiomers is displayed in Figure 1. The calculated (BLYP/SV(P) with the continuum solvent model for CHCl3) spectra of 2b 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 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 2b: H-1L 51% and H-1L 18% (see Figure 3 and SI). The second dominant 2b 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 2b). 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)-2b and (M, C)-2b enantiomers displayed mirror-imaged CPL spectra (Figure 2) with opposite g0 values ((P, A)-2b: +3.1 × 10^-3 and (M, C)-2b: -2.8 × 10^-3) around the emission maximum (~670 nm). These values are of the same order as for the 1b ligand enantiomers (g0 ~ ±10^-3) but lower than those of previously published planar[6]helicenes (g0 ~ ±10^-3), because Re orbitals are less involved in the helical π-system of the molecule (vide supra).
In order to improve the efficiency of the chiroptical and photophysical properties, tricarbonyl-isocyanide-helicene-bipy-Re\(^{1}\) complex M-3b was prepared (see Scheme 1) in 75% yield from either (M\(\text{A}^{\text{Re}}\))-(+)-2b\(^{1}\) or (M\(\text{C}^{\text{Re}}\))-(+)-2b\(^{2}\). In this complex, the Re center appeared labile and 3b was obtained as a mixture of (M\(\text{A}^{\text{Re}}\))-3b\(^{1}\) and (M\(\text{C}^{\text{Re}}\))-3b\(^{2}\) as observed by \(^{1}H\) and \(^{13}C\) 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 (\(\lambda_{\text{max}}\text{phos} = 598 \text{ nm}, \phi = 6\%, \tau = 79 \mu s\); 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\(\text{C}^{\text{Re}}\))-2b\(^{1}\) and (P\(\text{A}^{\text{Re}}\))-2b\(^{2}\) cationic diastereomeric mixture of Re\(^{1}\) complexes P-3b\(^{1,2}\) displays an additional positive CD-active band around 450 nm (\(\Delta \varepsilon = 17.5 \text{ M}^{-1} \text{ cm}^{-1}\)). 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 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 2b\(^{1,2}\) \([- (P\text{A}^{\text{Re}})-3b; |\psi_{1,3}\rangle = 15040 (\pm 5\%) \rightleftharpoons (C = 8.8 \times 10^{-3} \text{ M, CH}_2\text{Cl}_2); (M\text{A}^{\text{Re}})-(3b; |\psi_{1,3}\rangle = -14230 (\pm 5\%) \rightleftharpoons (C = 9.7 \times 10^{-5} \text{ M, CH}_2\text{Cl}_2); \text{calc. BHLYP Boltzmann average for 3b}^{1,2} \text{ conformers is } +14034 \text{ degree cm}^2/\text{dmol for the P-isomers, see SI}].

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). 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 BHLYP functional along with the Tamm-Dancoff approximation (see SI) resulted in much too high emission lifetimes (Table S6). 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 BHLYP may indicate that the metal orbital contributions 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 \textit{et al.}\(^{11}\) for organometallic complexes (full TDDFT with B3LYP functional), a dramatic improvement of the lifetimes and some lowering of the emission energies (to ~1.9 eV) was obtained (Table S7), 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\(^{1,2}\) to 3b\(^{1,2}\) is correctly reproduced with B3LYP and qualitatively consistent with lesser metal orbital participation (lesser MLCT character) in the T\(_1\) emission transitions for 3b\(^{1,2}\) as compared to 2b\(^{1,2}\) (see SI). 5,4a,b

Finally, mirror-imaged CPL spectra were obtained in CH\(_2\)Cl\(_2\) for (M\(\text{A}^{\text{Re}}\))-3b\(^{1,2}\) and (P\(\text{A}^{\text{Re}}\))-3b\(^{1,2}\) (Figure 2) with respective \(\Delta \mu\) values of -0.0015 and +0.0013. Overall, cationic Re\(^{1}\) complexes display similar CPL characterstics 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.

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.

Acknowledgments

We thank the Ministère de l’Education Nationale, de la
Recherche et de la Technologie, the Centre National de la Recherche Scientifique (CNRS), the ANR (10-BLAN-724-1-NCPCHEM) and 12-BS07-0004-METALHEL-01) and the LIA Rennes-Durham for financial support. This work has received financial support from the National Science Foundation (CHE 1265833 to J.A.) and the Foundation for Polish Science Homing Plus programme co-financed by the European Regional Development Fund (to M.S.). M.S. is also grateful for financial support via a Ministry of Science and Higher Education in Poland scholarship. We acknowledge the Center for Computational Research (CCR) at the University at Buffalo for their continuing support of our research projects. G.M. thanks the National Institute of Health, Minority Biomedical Research Support (1 S10 GM089589-05 and 3 S06 GM008192-27S1) and the Henry Dreyfus Teacher-Scholar Award for financial support.

Notes and references

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† Electronic Supplementary Information (ESI) available: synthetic, spectroscopic and computational details. See DOI: 10.1039/b000000x/8

* Note that enantiopure (+) and (-) complexes have been prepared by chiral HPLC and they displayed very weak CD activity (Δε max = 20 M⁻¹ 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 non-negligible even at 77 K. We assume that the non-radiative decay rates for the complexes are similar under these conditions.

