Chirality-at-rhenium complexes with a helicenic NHC ligand: synthesis, photophysical and chiroptical properties.

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Helicenes are made of $n$ ortho-fused aromatic or heteroaromatic rings. This helical structure thus formed can furnish inherent chirality and remarkable properties such as high optical rotation values (in comparison with chiral pool compounds). Helicenes were used as molecules displaying strong chiroptical properties[1] and as enantioselective ligands in asymmetric catalysis,[2] to name a few.[3] On the other hand, $N$-Heterocyclic Carbenes (NHCs) are a well-defined class of electron-rich ligands with a versatile skeleton tuneable on purpose, known to form strong metal-carbene bonds in organometallic complexes.[4] Recently, by combining these 2 chemistries, our group has been able to prepare iridium complexes with enantiopure helical carbene ligands which display long-lived light-green circularly polarized phosphorescence (1).[5] Following these results, we have interested ourselves on the design of helicenic $N$-2-pyridyl-NHCs and their use as chiral ancillary ligands in transition metal complexes. We have achieved the synthesis of complex 2 which possesses both helical chirality ($P/M$) and less common chirality-at-rhenium ($A_{Re}/C_{Re}$). All pure stereoisomers of 2 were obtained by chiral HPLC resolution and their photophysical (absorption, emission) and chiroptical properties (optical rotation, circular dichroism and circularly polarized luminescence) were examined. Interestingly, 2 exhibits green circularly polarized phosphorescence (Fig. 1) with a dissymmetry factor ($g_{lum}$) controlled by the configuration of the ligand and the metal center, following the trend described previously with 1.

Fig 1. CPL spectra of enantiomeric pairs ($P.C_{Re}$)/($M.A_{Re}$)-2 and ($P.A_{Re}$)/($M.C_{Re}$)-2 measured in degassed $\text{CH}_2\text{Cl}_2$ at r.t.