



## Luminescence modulation of rhenium complexes induced by the structural isomerism of their organic ligand

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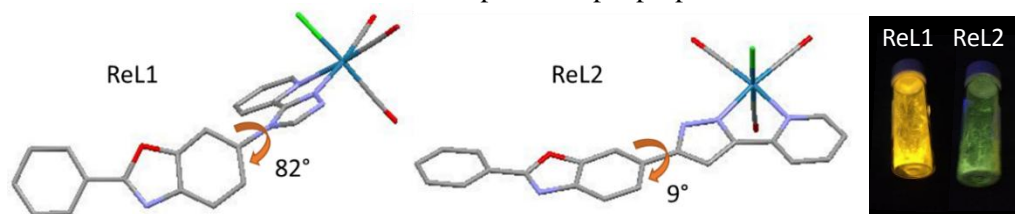
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### Introduction

Transition metal complexes which are weakly emissive when molecularly dissolved, but highly emissive when aggregated, have recently attracted intense research interest for applications in optics, optoelectronics and bio-imaging.<sup>1</sup> However, among them, the rhenium complexes have been scarcely studied. It is shown here that the simple structural isomerism of a chelating organic ligand in these complexes may significantly govern their electronic properties, and modify their aggregation-induced phosphorescence emission (AIPE) ability.

### Results and Discussion

This study focuses first on two very similar tricarbonyl Re(I) complexes **ReL1** and **ReL2**, each incorporating a different structural isomer of the pyridyl-triazole (pyta) ligand<sup>2</sup> connected to a 2-phenylbenzoxazole (PBO) moiety (Fig. 1). The X-ray structures indicate that in **ReL1** the PBO moiety and the pyta ligand almost form a right angle hindering the electron delocalization, while in **ReL2** their nearly planar arrangement favors the electron delocalization in the whole organic ligand. The geometry of these complexes deeply influences their electrochemical and optical properties. Indeed, in solution and in the solid state, the color and intensity of their phosphorescence emission is quite different, and only **ReL1** clearly exhibits an AIPE behavior. TD-DFT calculations are in good agreement with all the experimental data. In a second step, to improve the emission properties of our rhenium compounds, two new complexes have been prepared. **ReL3** presents a PBO moiety substituted by a bulky group. **ReL4** is an isomer of **ReL1** in which the PBO moiety is now linked via its phenyl group to the pyta fragment. A comparison with the first two complexes thereby allows the impact of the new structural modifications on the spectroscopic properties to be evaluated.



**Figure 1.** From left to right: Molecular views of **ReL<sub>1</sub>** and **ReL<sub>2</sub>**; Pictures of the complexes in the solid state under UV light (365nm).

### Conclusion

This comprehensive study aims to rationalize the links existing between the intimate nature of the pyta-PBO ligands and the electronic properties of their corresponding rhenium complexes.<sup>3</sup> It paves the way for a new generation of AIPE-active compounds that associate good emission efficiency to the intrinsic advantages of tricarbonyl rhenium complexes, i.e. stability, versatility and biocompatibility, in view of bio-imaging applications.

### Bibliography

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<sup>3</sup> J. Wang *et al.* The unsuspected influence of the pyridyl-triazole ligand isomerism upon the electronic properties of tricarbonyl rhenium complexes: An experimental and theoretical insight. Submitted for publication.