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2-PHENYLBENZOTHAZOLE CYCLOPLATINATED(II) COMPLEXES WITH PICOLINATE LIGANDS. POLYMORPHISM AND REVERSIBLE MECHANOCROMIC BEHAVIOR

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Cyclometalated Pt^{II} complexes have received great interest due to their potential application in fields as organic light emitting diodes (OLEDs), dye-sensitized solar cells (DSSC), hydrogen production, chemical sensing and bioimaging. The square-planar geometry and the coordination of flat and delocalized ligands favors Pt···Pt and /or $\pi\cdots\pi$ intermolecular interactions, able to generate extended chains and/or oligomeric nanostructures displaying, in occasions, polymorphs with distinct stacking arrangements in solid state with modification of their optical properties. These interactions are sensitive to external stimuli and some of these complexes display mechanochromic and/or vapochromic behavior [1].

Here, we present new luminescent Pt^{II} complexes with 2-phenylbenzothiazole (pbt) as cyclometalated ligand and two different picolinate ligands [Pt(pbt)(R-pic-N,O)] (R= H **1**, OH **2**). Both of them present mechanochromic behavior with high-contrast emission changes and complex **2** exhibits polymorphism in solid state due to the presence of the OH substituent, that allows to modulate the packing through donor-acceptor H-bonding interactions with the CH₂Cl₂ solvent molecules. Three pseudopolymorphs of **2** were isolated including yellow (**2-Y**), orange (**2-R**) and black one (**2-B**) with emission in the range of the visible to the near infrared. Single crystal studies show that **1** and **2-Y** present a columnar stacking with only weak $\pi\cdots\pi$ interactions, whereas the **2-R** polymorph displays aggregated 1D infinite chains with both Pt···Pt and $\pi\cdots\pi$ interactions. To insight in the nature of the optical properties of the different polymorphs, theoretical calculations (DFT/TD-DFT) of different oligomers have been studied, indicating relevant Pt···Pt interactions, particularly in their T₁ states, associated with a metal-metal to ligand charge transfer transition. Additionally, Noncovalent Interaction (NCI) studies have been carried out.

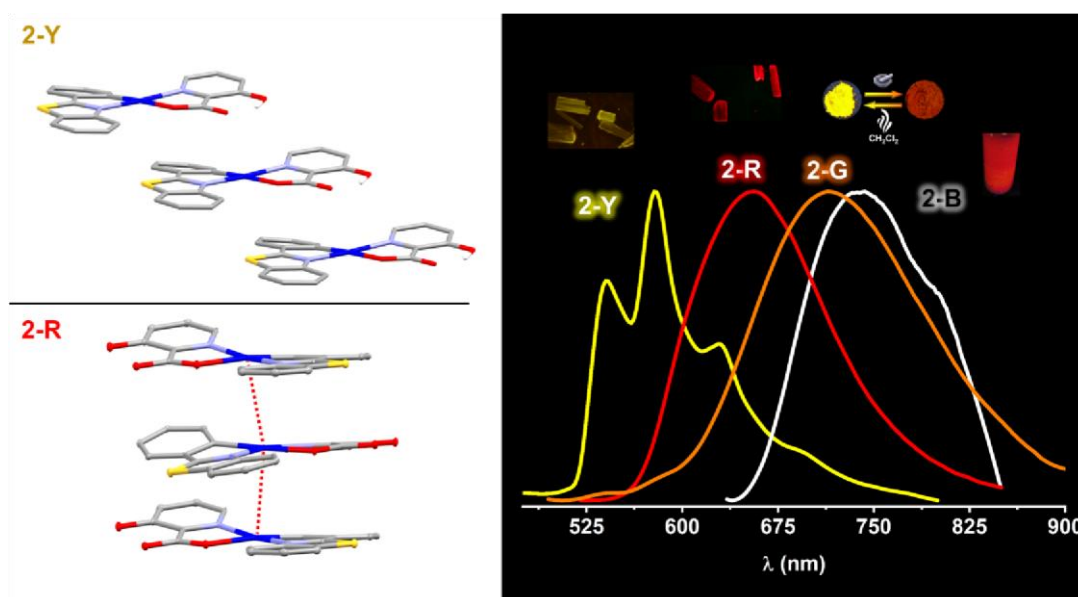


Figure 1. Polymorphism and mechanochromism behavior of complex **2**.