

LUMINESCENT CYCLOPLATINATED SYSTEMS BASED ON THE 2-PHENYLBENZOTHAZOLE LIGAND: RELATIONSHIP BETWEEN STRUCTURE AND OPTICAL PROPERTIES

David Gómez de Segura, Rebeca Lara, M^a Teresa Moreno and Elena Lalinde

Departamento de Química-Centro de Síntesis Química de La Rioja (CISQ), Universidad de La Rioja, 26006, Logroño, ESPAÑA
 daseguz@unirioja.es

Over last few decades phosphorescent cyclometalated Pt^{II} complexes have received expanding interest due to their potential utility in optical devices, photochemistry, sensors or biological imaging¹. In many occasions the light emitting behaviour of molecular solids, rigid media and concentrated solutions of these complexes differ from their dilute solutions because the occurrence of easy stacking of molecules. In particular, the coordination of flat and delocalized ligands favors Pt···Pt and/or π ··· π intermolecular interactions, able to produce extended linear chains and oligomeric nanostructures, which display a rich polymorphism in solid state with alterations in their optical properties.² These interactions are sensitive to external stimuli and some of these compounds present mechanochromic or vapochromic behaviour.

In this work we describe new Pt^{II} compounds based on the 2-phenylbenzothiazole (pbt) fragment as cyclometalated group and bidentate auxiliary ligands L^X, type [Pt(pbt)(L^X)] [L^X: PPh₂(*o*-PhCOOH) **2**, PPh₂(*o*-PhSO₃H) **3**, PPh₂{(CH₂)₂COOH} **4**, picolinic acid **5** and 3-aminopicolinic acid **6**], prepared from the DMSO precursor [Pt(pbt)Cl(DMSO)] **1**.

X-ray diffraction studies show structures self-assembled by hydrogen bonding and/or π ··· π intermolecular interactions. Interestingly, **6** shows two solid phases, depending on the crystallization solvent, which display different colors (red and black) and distinct emissions and **5** is mechanochromic. To insight into the nature of the optical properties, theoretical analysis have been carried out at DFT/TD-DFT level for selected complexes and for **5**, a dimer model (**5**₂) has been studied to examine the Non-Covalent Interactions (NCI).

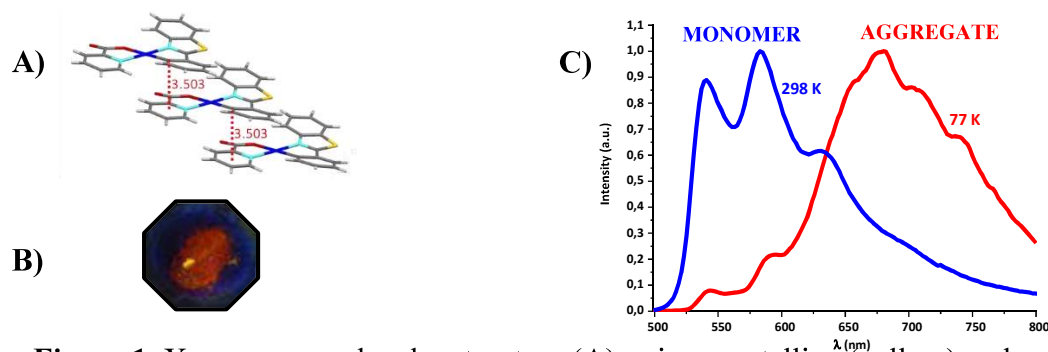


Figure 1. X-ray supramolecular structure (A), microcrystalline (yellow) and ground (orange) solid (B) and emission spectra in CH₂Cl₂ (298 K and 77K) (C) of **5**

Key words: Luminescent, Platinum, Cyclometalated, Aggregation.

Acknowledgments: We thank Spanish Ministerio de Ciencia e Innovación (Project: PID2019-109742GB-I00) and Gobierno de La Rioja (Project: ADER2017-I-IDD-00046)

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