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Electronic Tuning of the Cycloplatinated(II)-Thiolate Complex through Borane Interaction in the Secondary Coordination Sphere

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Cycloplatinated(II) complexes are one of the noteworthy classes of organoplatinum(II) compounds with impressive photophysical properties that are structurally and electronically tunable through supporting ligands [1]. For example, thiolates play important roles in the capacity of tuning both steric and electronic properties of transition metal complexes as supporting ligands by coupling strong σ-donating, which would make the metal center more electron-rich (based on the electron-donating ability of the aromatic ring coordinated to the S atom) and hence promote the luminescence properties of the complexes by increasing the energy of the *dd** states [2]. Commonly, the usual modification of a complex is brought on by one or more covalent modifications to the supporting ligand environment, requiring ground-up synthesis of the modified ligand and complex. But beyond that, postsynthetic addition in order to modify Lewis acid-base interactions is a synthetic strategy that complements covalent modification and tunes the optical and electrochemical properties of cycloplatinated(II) complexes. This technique of tuning is more rapid and methodical than that offered by the usual covalent substituent modification [3].

In this work, we're up to demonstrate the concept that borane-pyridine thiolate Lewis acid-base interactions in the secondary coordination sphere can bring about significant and systematic changes in the photophysical properties of cycloplatinated(II) complexes bearing the ppy (2-phenylpyridine) as a cyclometalated ligand with the general formula [Pt(ppy)(κ^1-S-Spy)(PPh_3)], where Spy = 4-pyridine thiolate and PPh_3 = triphenylphosphine. The complex was titrated with BPh_3 as a Lewis acid at room temperature and was finally primarily identified by NMR, HR ESI-MS, and X-ray crystallography. UV-Vis and photoluminescence spectroscopies were applied in order to conduct photophysical investigations (Figure 1), and the obtained results were rationalized with the help of DFT (density functional theory) calculations.

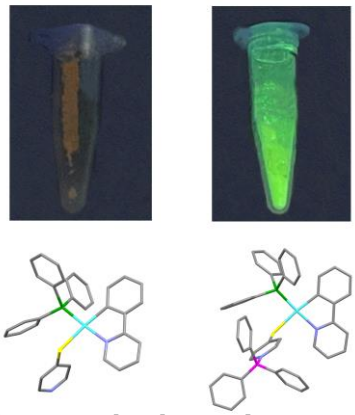


Figure 1. The chemical structures of Pt(II) complexes (down) and their emission under a UV lamp (up).

Keywords: Cycloplatinated complex, Photophysical properties, Thiolate ligand, Borane.

References

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