Poster Presentation
Inter-Disciplinary Explorations in Chemistry (I-DEC 2018)

"Ligand Dependent Excited State Character of Rhenium(I)-Carbonyl-Diimine Complexes"

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Abstract: The relation between structure and property of excited states of rhenium(I) carbonyl-diimine complexes is intriguing. While the orbital parentage of the low-lying excited state – MLCT, LLCT, ILCT, or $\sigma \rightarrow \pi^*$ - is determined by the axial ligand, the excited state properties like lifetime, energy, reactivity, decay mechanism are determined by both axial and diimine ligands. The exceptionally diverse photophysical and photochemical behavior of rhenium(I) complexes depends on the nature of low-lying excited states. The excited state properties can be tuned by judicious choice of diimine and axial ligands. Hence, an understanding of the excited state character of these compounds becomes important in order to use them in applications such as light emitting devices, sensors, probes for photo-polymerization, optical switches etc. These complexes can also exhibit solvatochromism leading to a reordering of energy levels with change in the polarity of solvents.

In the present work, we have synthesized rhenium(I) complexes with different diimine and axial ligands. The varying nature of excited states, especially the MLCT and LLCT states, with change in these ligands have been studied by absorption, fluorescence, resonance Raman and time resolved absorption spectroscopic techniques. The ground state resonance Raman spectra exhibit an enhancement of different modes on excitation across the lower energy absorption band. Time-resolved absorption spectra show varying lifetimes in solvents of varying polarity. These observations are indicative of a mixed MLCT/LLCT character.

References and Notes:

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