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Review

Probing the excited state nature of coordination complexes with blended organic and inorganic chromophores using vibrational spectroscopy

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ABSTRACT

The use of transient vibrational spectroscopy in the analysis of rhenium(I) and ruthenium(II) complexes is discussed. Particular focus is given to the use of resonance Raman spectroscopy to probe initial photoexcitation and transient resonance Raman and infrared spectroscopy to observe subsequent relaxation processes. Several types of excited states are accessible for these systems, which can be probed on a range of timescales by these techniques. These include ligand-centered π,π^* , intraligand charge

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transfer, and metal-to-ligand charge transfer; a number of these states may be overlapping and show mixing. As such, these techniques are described in some detail and their utility is given by discussion of examples in which the electronic complexity of the system increases from systems which are metal-to-ligand charge-transfer through to systems which have complex interplay between intraligand and metal-to-ligand charge transfer states. Particular attention is paid to complexes containing $[\text{Re}(\text{CO})_3(\text{L})(\text{N}^{\wedge}\text{N})]$ metal centers and dipyrrodo[3,2-a:2',3'-c]phenazine ligands, as subtle structural changes on these often manifest in significant changes in the photophysical properties and they are therefore well-suited to the investigation of excited states. The use of these complexes in areas such as solar energy conversion and the probe of biological systems are also discussed.

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1. Introduction

Metal polypyridyl complexes have found utility across a range of applications that include: solar cells [1,2], sensors [3–5], organic light-emitting diodes [6–9], and photocatalysts [10–13]. The photophysics of many d^6 metal polypyridyl complexes are dominated by MLCT excited states. This state results in the metal being formally oxidized and the polypyridyl ligand being reduced. For many of these complexes this is both the dominant low energy chromophore and the lowest excited state. The energy of the MLCT emission of the complexes can be linearly correlated with the difference between electrochemical potentials for first oxidation and first

reduction ($E_{1/2}$) [14]. The $E_{1/2}$ showed a linear relationship to the Hammett σ constants for the substituents. This is reasonable as the MLCT state (Fig. 1) is the formal oxidation of the electron donor (the metal) and the reduction of the electron acceptor (the ligand). In addition, in a system in which the photophysics are dominated by a single excited state, which is MLCT in nature, then it is possible to derive good correlations between the excited state lifetime (τ) and the nonradiative decay rate constant (k_{nr}) and the energies of the excited state and the structural distortion caused upon excitation [15]. It is possible to engineer long-lived MLCT excited states with low energies by using ligands that have small structural distortions on reduction (population of the MLCT state) [16].

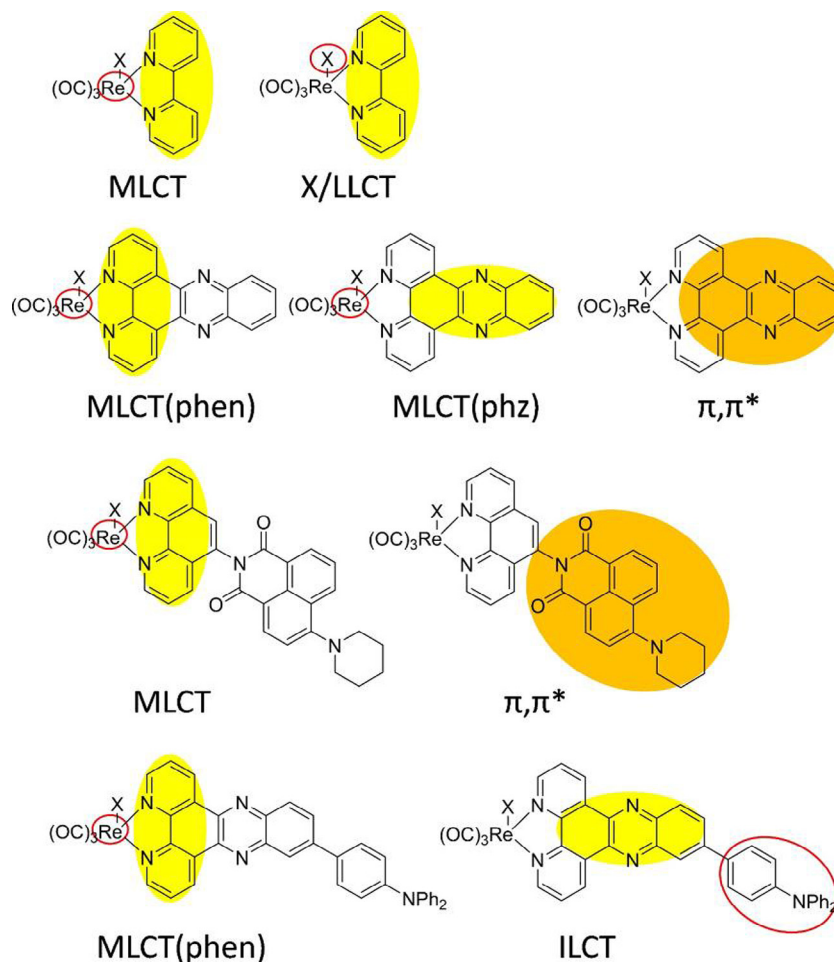


Fig. 1. Depiction of the types of excited states derived from a number of multichromophore systems based on $\text{Re}(\text{CO})_3\text{X}(\text{N}^{\wedge}\text{N})$. Electron donors are shown with open circles, acceptors with filled yellow oval. π, π^* states in orange ovals.

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