

Development of a new class of ruthenium polypyridine photo-redox assemblies

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A new class of ruthenium terpyridine complexes incorporating imine functionalities, $[\text{Ru}^{\text{III/IV}}(\text{trpy})(\text{L})\text{Cl}]$ ($\text{L} = o\text{-OC}_6\text{H}_3(\text{R})\text{-C}(\text{R}\text{C}=\text{N-CH}_2\text{-Ar}$ or $o\text{-OC}_6\text{H}_3(\text{R})\text{-C}(\text{R}\text{C}=\text{N-NH-Ar})$) have been developed as possible effective photo-redox assemblies. The imine functions incorporating NH spacer have undergone imine to azo tautomerism on coordination to the ruthenium terpyridine moiety whereas the imine functions (L) having CH_2 spacer remain unaltered on coordination. A significant shift in MLCT band energy has been observed depending on the field strength of coordinated L. The complexes display reversible $\text{Ru}^{\text{III}}\text{-Ru}^{\text{II}}$ and quasireversible $\text{Ru}^{\text{IV}}\text{-Ru}^{\text{III}}$ couples. The effect of internal imine to azo transformation of L has been well-reflected in the redox behaviour of the metal complexes. The complexes exhibit moderately strong emissions from the lowest energy MLCT bands in the range 661–690 nm in EtOH-MeOH (4:1 v/v) at 77 K. The quantum yields of the complexes are found to vary significantly depending on the nature of L as well as the substituents present in the framework of L. Electronic structures of the trivalent complexes indicate the presence of high degree of rhombicity in the complexes. In the presence of Ag^+ ion, the replacement of Cl^- ion takes place with concomitant metal oxidation followed by antiferromagnetically coupled mono dimer formation, $(\text{trpy})(\text{L})\text{R}^{\text{III}}(\text{mO})\text{Ru}^{\text{III}}(\text{L})(\text{trpy})$.