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Title:	Design and Development of first row transition metal based photocatalyst supported by redox-active ligand
Authors:	Singh, Kirti
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Abstract:	<p>Abstract: Over the last two decades, photochemistry has emerged as a powerful tool for synthesis of fine chemicals using inexhaustible, safe, inexpensive and sustainable source of light; solar energy. While the area of photocatalysis is dominated by precious 4d and 5d metals owing to their long-lived excited state and high excited-state redox potential, the development of base metal photocatalyst is on a surge. In this seminar, we will report photocatalyst of 3d metals, Zn(II) and Cu(I), relying on redox non-innocence of coordinated ligands for photoinduced electron transfer. We report the synthesis and characterisation of homoleptic Zn(II) complex of β-diketiminato ligand and its application for functionalization of olefins. We have performed a series of spectroscopic investigation to understand the excited state dynamics of the molecule. Under blue light, the molecule efficiently catalyses atom transfer radical addition of styrene via reductive quenching pathway. We have performed several control experiments to delineate the mechanism supported by DFT calculations. Furthermore, from the calculated excited state potentials and redox non-innocent nature of ligand, we anticipate the photocatalyst to undergo photo-oxidation and exhibit bimodal behavior. We show that under visible light, the metal complex catalyses trifluoromethylation of various arenes and heteroarenes via oxidative quenching of the molecule. The mechanistic investigation revealed that the redox equivalent to catalyse the photoinduced trifluoromethylation is afforded by the ligand backbone. Encouragingly, the solid-state emissive nature of the zinc complex was utilized to fabricate solution processable, multi-layered OLED device emitting in the yellowish-green region. Additionally, a dimeric Cu(I) complex of pyrazole-based ligand will be reported which sheds light on the effect of Bronsted acid on the excited state of photocatalyst. We have utilized the catalyst to carry out demethylation and further synthesis of tetrahydroquinolines. The nitrogen rich ligand was found to be proton responsive that mediates the photoinduced electron transfer in excited state.</p>
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