INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: "***Investigation on Transition Metal-Radical Complexes for Oxidative Cleavage of Aromatic C–C Bond, Aliphatic C–N Bond and Radical-to-Metal Electron Transfer Phenomena***"

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SHORT ABSTRACT

Aminophenol-containing non-innocent ligands and their corresponding transition metal complexes are very useful for enzymatic functional mimicking; homogeneous catalysis, *e.g.* $-CF_3$ group transferring, C–N bond forming reactions; molecular oxygen activation; etc. In these regards, three new aminophenol-based redox active ligands [**H_2Gan^{AP}**, **$H_4L^{Piperazine(AP/AP)}$** and **$H_2L^{AP(Ph)}$**] and their corresponding transition metal complexes have been investigated**.** Reaction of ligand **H_2Gan^{AP}** with an Fe(II) or Fe(III) perchlorate salt in the presence of dioxygen provided complex **2A** which led to a biomimetic C–C bond cleavage of the aromatic ring of the 2-aminophenol unit. On the other hand, a different reactivity (no C–C bond cleavage of the aromatic ring) was observed when Mn(II) perchlorate salt was employed in the reaction thereby provided complex **2C.** The difference in the reactivity emphasized the importance of the spin and the nature of the metal-radical interactions in controlling the dioxygen reactivity of transition metal complexes involving non-innocent ligand. The piperazine based ligand **$H_4L^{Piperazine(AP/AP)}$** provided an octahedral Co(III) complex (**3A**) where the coordinated ligand was present in non-radical aminophenolate form due to the presence of hydrogen bonding interaction. Contrarily, iminosemiquinone radical was generated for both the Cu(II) complex(**3B** and **3C**) when there was no such hydrogen bond interactions. Thus, the effect of hydrogen bonding and the orientation of the ligand framework have been demonstrated for the formation of radical and non-radical transition metal complex. A facile redox process of **$H_2L^{AP(Ph)}$**-containing five coordinate diradical Co(III) complexes (**4C** and **4D**) and four coordinate monoradical Co(III) complex (**4A**) and the redox interconversion have been achieved in presence of sunlight. The complexes were being utilized in the catalytic conversion of isocyanate to urea. This study established the potential of radical-coordinated transition metal complexes in photocatalysis. One step synthesis of five-coordinate square pyramidal Cu(I)-bis(iminoquinone) complex (**5B**) has also been successfully carried out by using non-innocent ligand **$H_2L^{AP(Ph)}$** and excess amount of $CuCl_2 \bullet 2H_2O$ salt via geometry-driven iminosemiquinone radical to Cu(II) center electron transfer. Furthermore, it was found that complex (**5B)** oxidized KO_2 to dioxygen molecule.