Abstract and Keywords

From respiration to photosynthesis, many of the most challenging chemical transformations are occurred by natural enzymes which use two or more metal centers working together in perfect harmony of electronic and redox synergy. However, this powerful concept of redox and electronic synergy in bimetallic complexes has been underexplored for various challenging chemical transformations due to a lack of design principles and the synthetic difficulties associated with bimetallic complexes. In this context, this thesis explores the design and engineering of monometallic and homo-bimetallic catalysts capable of addressing CO_2 reduction, and further extends this strategy to the development of homo- and hetero-bimetallic catalysts for controlled radical polymerization. Firstly, Cu(I/II) complexes supported by redox-active NNN di(picolyl)amine ligands were developed to selectively activate CO_2, enabling the formation of rare C_2 products through a nucleophilic, multi-electron pathway *via* bimetallic intermediates. Additionally, the cleavage of $C(sp^3)$-$C(sp)$ bond of the Me-CN molecule was achieved by the multi-nuclear phenanthroline-based Cu(II) carbonate complex, showcasing the efficacy of cooperative effect of the homonuclear complexes. By extrapolating NNN framework, we attempted to construct a heterotopic ligand by tailoring terpyridine unit. The unorthodox phosphine functionalization guided the synthesis novel Ru(II)–Fe(II) heterobimetallic complex. This complex was strategically employed for atom transfer radical polymerization (ATRP), where the existing redox synergy between the two metals played a vital role allowing excellent control, high conversion, and narrow polydispersity index in produced acrylate polymers by maintaining the active and dormant species. The extended work on the Ru(II)-Fe(II) heterobimetallic system was further refined by minimizing the metal-metal distance from 14.2 Å to 7.69 Å, which significantly enhanced intramolecular electron transfer and resulted in noticeably higher monomer conversion rate during ATRP process. Inner-sphere electron transfer and intramolecular electron transfer were sketched in these synthesized Ru(II)-Fe(II) HBC. Cost-friendly Fe(III)-based homo-bimetallic photocatalysts were designed to utilize ligand-to-metal charge transfer excited states under blue light, catalyzing controlled polymerization without external halide additives, and making a practical solution as a bench-stable catalyst. Overall, this work reveals that redox and electronic synergy is a crucial feature that governs catalytic efficiency, enabling breakthroughs in CO_2 transformation and controlled radical polymer growth.