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Title:	Mechanistic investigation of multielectron redox process employing redox- active ligands
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Abstract:	<p>Non-innocent redox-active ligands are at the heart of 2e<sup>-</sup> chemistry steered by sequential 1e<sup>-</sup> reactions. Bimodal functionality accomplishing various complex redox-neutral transformations is enabled by easier access to diverse redox states of such ligands. Notably, several redox- active cofactors are used by nature to carry out the redox-chemistry of biological adaptations. It's of greater interest to get mechanistic insights into such chemistry, as it aids in simulating many biological systems and resolving essential concerns about their compatibility with introduced drugs. In this direction, a substantial amount of work demonstrated the addition-elimination or transamination pathway for alcohol dehydrogenation that mimicked quinone-containing cofactors. Despite the possibility of a one-electron reduction in the cofactor motif, such routes are known to be governed by two-electron processes. In striking contrast to previously established approaches, we provide a one-electron approach to quinone catalysis for dehydrogenating alcohols in Chapter 2. The process commences with the photoexcitation of a dione motif, which is then photo-reduced by KO<sup>t</sup>Bu, producing a persistent semiquinonate radical. Alcohol binds to the backbone of the quinone, forming a hemiacetal intermediate that leads to a critical hydrogen atom transfer (HAT) step, which accomplishes the dehydrogenation. A series of kinetic investigations, including the Bell-Evans-Polanyi correlation with the bond dissociation free energy, proved that the HAT is rate-determining during dehydrogenation processes. The kinetic isotope effect is substantial at room temperature (7.7), implying considerable tunneling contribution. A culmination of several experiments affirms the radical-mediated one-electron pathway to be operative, which is in striking contrast to two-electron-driven quinone catalysis established so far. Moreover, our keen interest in ligand-mediated base-metal catalysis encouraged us to look for alternative ligands with a backbone capable of multielectron alterations without inflicting irreversible bond cleavage. In chapter 3, we chase a tunable and redox-active 'NNN' pincer backbone to decode the plausibility of reversible chemical changes on the ligand so that it can drive some catalytic reactions. Upon metalation, the fully reduced iminocatechol form undergoes facile aerial oxidation, yielding the iminosemiquinonate redox state. Substantial changes in the UV-Vis absorption spectrum manifest an equilibration process in the solution phase to generate the active form of catalyst. This active form is attacked by Grignard reagent forming an electron-rich species. The iminosemiquinonate backbone in this species is robust to do a SET activating aryl-bromide bond to form iminoquinone backbone and aryl radical. The aryl radical attaches to the metal centre through an escape-rebound route, and reductive elimination produces the desired cross-coupled product. Although the synthesis of complex began with the catecholate form, the redox chemistry is entirely governed by a reversible iminosemiquinonate to iminoquinone redox couple. Due to high abundance and cheaper costs, base-metal mediated photocatalysts have garnered attention in recent times. There are literature precedences about Brønsted acids accelerating the photocatalytic activity of complexes. In Chapter 4, we probe the effects of TFA on Cu- catalyzed demethylation reactions. Interestingly, TFA acts as a source of proton to bind on catalyst's ground state. The introduced geometry distortion upon protonation enables DMA to have an inner-sphere interaction before photoreducing the excited state of PC. The proximity of DMA refutes the well studied oxidative quenching pathway, where metal adopts change in its oxidation state.</p>
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