Control of Electron Transfer for Efficient Oxygenation Reactions

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Electron transfer is the most fundamental reaction to govern chemical reactions. To find an effective way to control electron transfer, electronic structures of key active species were investigated in detail with various techniques including absorption, ^{1}H and ^{2}H NMR, EPR, IR resonance Raman spectroscopy and magnetic susceptibility measurements. Correlations between electronic structures and electron transfer ability are the main focus.

1. Design and Synthesis of Photoactive Salen-Type Ligands

Salen-type ligands are well known as the most versatile framework for catalysts, because of the simple structure that is suitable for large-scale preparations and chemical modifications. The present study investigated a new method to incorporate excellent photochemical properties without sacrificing structural advantages of salen-type ligands.

The key concept is tautomerization of a salicylidene ring of a salen-type ligand, which converts a phenolate structure to a quinoidal structure. The resulting quinoidal salen-type ligand is expected to show better photochemical properties, because quinones having a quinoidal structure are excellent photocatalysts.

To compare photochemical properties of salen-type ligands in a quantitative manner, fluorescence properties of salen-type ligands with redox-inactive zinc(II) ion were investigated. One of the achievements is a finding that the steric bulk of a substituent on salicylidene rings in addition to the molecular space around the diamine moiety plays a critical role for high fluorescence emission efficiency. Another point is an electron-donating or electron-withdrawing substituent on salicylidene rings, which systematically alters an absorption/fluorescence wavelength.