

Laboratory of Functional Organic Chemistry

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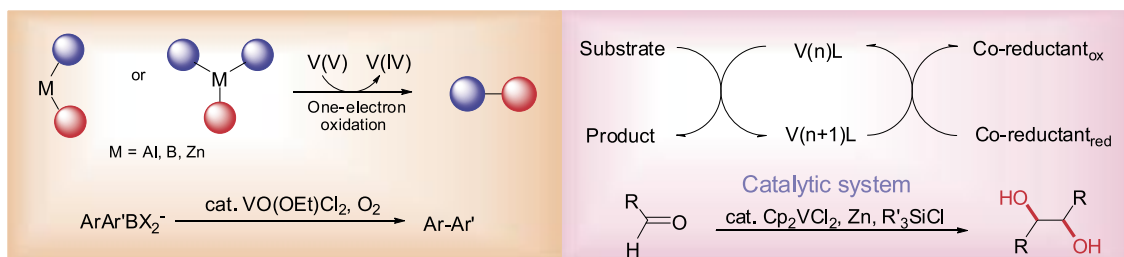
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Efficient bio-inspired redox systems are created for organic synthesis and materials synthesis.

Novel Synthetic Reactions via Electron Transfer

The one-electron oxidation capability of oxovanadium (V) compounds has been demonstrated to induce synthetically useful oxidative transformations. Selective carbon-carbon bond formation occurs via ligand coupling through intermetallic interaction between vanadium species and main-group organometallics. Organoborates undergo catalytic selective coupling under oxygen. Bio-inspired (bromoperoxidase) and environmentally benign vanadium-catalyzed bromination can be achieved in aqueous media with the use of H_2O_2 , HBr, and KBr.

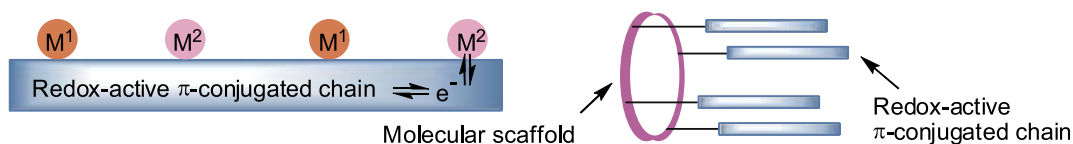
Low-valent vanadium and titanium are useful in reductive transformations. Catalytic reactions for one-electron reduction have been achieved by using multi-component catalytic systems. For example, the catalytic pinacol coupling provides a useful method for diastereoselective C-C bond formation.



Hybrid π -Conjugated Systems

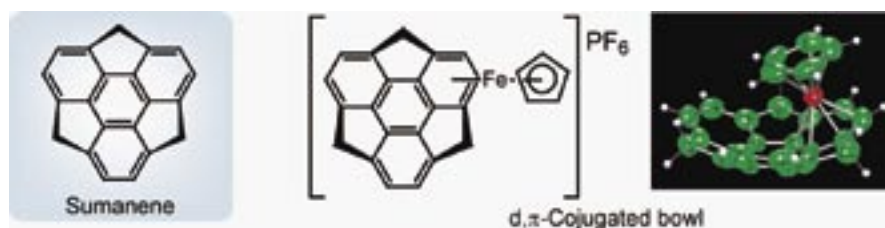
Hybrid systems composed of redox-active π -conjugated molecules, or polymers such as polyaniline with transition metals, are constructed to display the unique potential field depending on both redox properties. Electronic communication between the units is considered to be possible in these systems. Structural control of the complexation has been demonstrated to give nano-space-controlled d, π -conjugated systems. Chirality induction is attained in the π -conjugated chain by chiral complexation. These complexes are applied to efficient catalysts and electronic materials. The thus-organized conjugated palladium(II) complex is reduced to a small and well-dispersed nanoparticle.

Using a porphyrin and the corresponding zinc complex as a molecular scaffold provides a dimensionally oriented π -conjugated system bearing π -conjugated pendant groups. The structural and electronic characteristics are found to depend on the atropisomers bearing the $\alpha\alpha\alpha\alpha$ and $\alpha\beta\alpha\beta$ pendant groups. These systems are of potential in photoinduced electron transfer. Sandwich-type π -conjugated systems can also be constructed by complexation of the zinc porphyrin with a bridging ligand.



Bowl-shaped π -conjugated “sumanene”, which possesses a key partial C_{3v} symmetric structure of fullerene, has been synthesized for the first time. π -Extended π -bowls have been synthesized through condensation of the sumanene trianion with aryl aldehydes. A concave-bound iron complex is synthesized

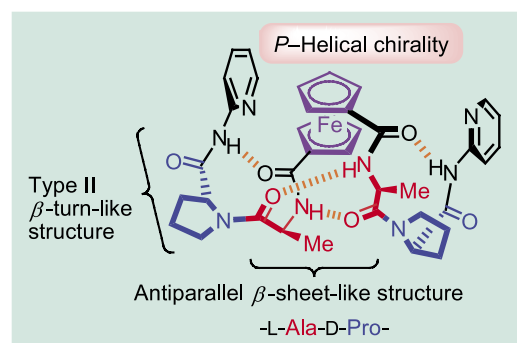
by ligand exchange between a cyclopentadienyl ring of ferrocene and sumanene. The concave π -bent surface serves as a ligand to give the corresponding d, π -conjugated bowl.



Biorganometallic Conjugates

A combination of ferrocene as a central reverse-turn scaffold with a dipeptide unit has been demonstrated to induce antiparallel β -sheet-like, type II β -turn-like, and γ -turn-like structures depending on the chirality and sequence. This architectural control of dimensional structures utilizing minimum-sized peptide chains possessing chiral centers and hydrogen bonding sites is a versatile approach to artificial, highly ordered systems. Size-selective and chiral molecular recognition of dicarboxylic acids has been achieved. Crystal engineering in biorganometallic chemistry is being developed.

Redox-active ferrocenes bearing a long alkylene chain are designed to be aggregated along the backbone of double helical DNA to produce redox-active (outer) and hydrophobic (inner) spheres around the double helical core. Dipeptidyl urea composed of two dipeptide chains has been synthesized to form the chiral hydrogen-bonded duplex in both solid and solution states.



References

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