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Conjugated Complex System Composed of Quinonediimine Unit

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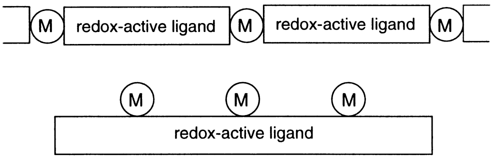
Summary: A combination of transition metals and π-conjugated molecules or polymers as redox-active ligands affords the hybrid conjugated complexes. A variety of structural design is possible based on the coordination number and geometry to construct an efficient multi-redox system.

Introduction

A combination of transition metals and π-conjugated molecules or polymers as redox-active ligands is envisaged to afford the hybrid conjugated complexes. Electronic communication is considered to be allowed by d,π-conjugation between metals and π-conjugated chains, forming a multi-redox system.[1] A variety of structural design is possible based on the coordination number and geometry to construct such a system. The system is essential to develop versatile functionalized materials and catalysts for electron transfer based on both relevant redox function. If the ligand possesses more than two coordination sites, two systems are allowed to be formed at least as shown in Scheme 1. Multi-coordination with a redox-active ligand affords the multi-nuclear complex. In the case of both metals and ligands possessing two coordination sites, these units are arrayed alternatively to give the corresponding polymer complex with a linear structure. Depending on their geometry, a cyclic complex is also allowed to be formed.

Scheme 1



Complexes with Redox-Active π-Conjugated Polymers

π-Conjugated polymers have received wide interest due to their high potential in a

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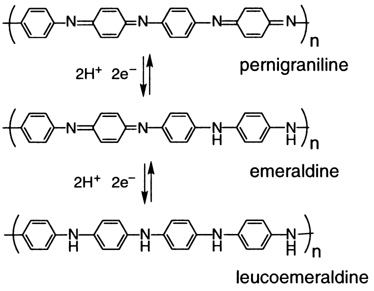
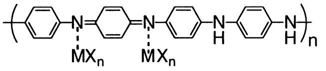
variety of application to electric materials as conducting polymers. π-Conjugated polymers exist in various redox states, as exemplified by pernigraniline, emeraldine, and leucoemeraldine bases of polyaniline (Scheme 2), and are capable of serving redox-active ligands to afford conjugated complexes. For example, the quinonediimine moieties of the emeraldine derivative undergo coordination to transition metals to give the conjugated complex **1**.

Scheme 2





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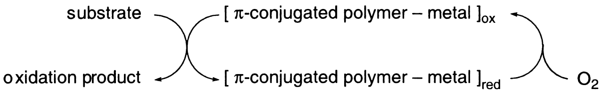
The complex of polyaniline with copper(II) chloride or iron(III) chloride has been found to catalyze the dehydrogenation reaction of cinnamyl alcohol into cinnamaldehyde.[2] Both components are essential for the catalysis. The catalytic system is applicable to the decarboxylative dehydrogenation of mandelic acid to produce benzaldehyde. A reversible redox cycle is achieved under oxygen atmosphere as shown in Scheme 3. In the redox processes of polyaniline, the reduced species is considered to be stabilized by complexation, indicating that the copper salt also serves as a dopant like protonic acid.[3]

Scheme 3



The redox interaction between metals and redox-active ligands largely contributes to a smooth reversible redox cycle in the transition metal catalyzed oxidation reactions. Actually, the Wacker oxidation reaction of a terminal alkene proceeds catalytically in the presence of a catalytic amount of polyaniline or polypyrrole derivative as a co-catalyst in acetonitrile-water under oxygen atmosphere to give 2-alkanone.[4] The redox processes of the π-conjugated polymer have been investigated by monitoring the CT band of the emeraldine base. The solubility of the complex catalysts depends on the substituent of the polymer, which allows to provide a homogeneous or heterogeneous catalytic system.

The controlled complexation of polyaniline derivative is performed in organic solvent.[5] The ratio of the *o*-toluidine unit of the emeraldine base of poly(*o*-toluidine) to the palladium(II) unit depends on the coordination number of the palladium(II) unit available for complexation with the quinonediimine moieties. Two coordination sites are employed for complexation in the case of $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$, affording a hybrid synthetic metal-transition metal conjugated network system **2** via crosslink (Figure 1). Only one coordination site is available for the palladium(II) complex **4** bearing the tridentate ligand, *N,N'*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide,[6] which provides a conjugated single-strand system **3**.

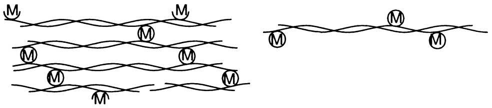


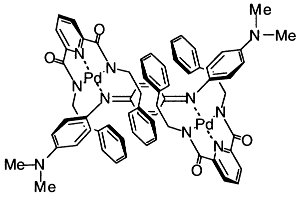
Figure 1 Conjugated network system **2** and conjugated single-strand system **3**.

The emeraldine base of poly(*o*-toluidine) undergoes oxidative complexation to VCl_3 to give the corresponding conjugated complex via reduction of the quinonediimine moieties along with oxidation of V(III) to V(IV).[7] The vanadium species is considered to serves as a metallic dopant and one-electron reductant.

Heterobimetallic conjugated complexes, in which an electronic interaction between different metals is permitted through a π-conjugated chain, have been readily prepared, for example, by successive treatment of poly(*o*-toluidine) with $Cu(OAc)_2$ and $Pd(OAc)_2$.[8]

Complexes with Redox-Active π-Conjugated Molecules

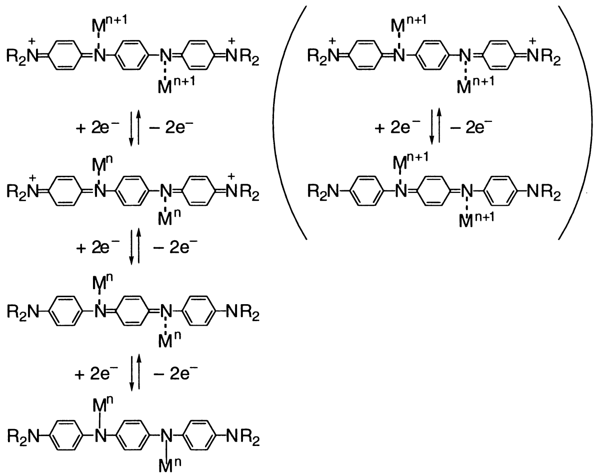
The coordination of the π-conjugated molecule **5**, *N,N'*-bis(4'-dimethylamino-phenyl)-1,4-benzoquinonediimine[9] to the palladium(II) complex **4** leads to the formation of the 1:2 conjugated palladium(II) complex **6**, which is considered to be a model complex for the above-mentioned polymer complexes.[10] Two palladium units are bridged by the quinonediimine moiety of **6**. The X-ray crystal structure of the isolated C_2-symmetrical complex **6*anti*** reveals the *anti* configuration of the bridging π-conjugated spacer.



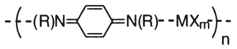
6*anti*

The conjugated complex **6** exhibits three separate redox waves assignable to the successive one-electron reduction processes of the quinonediimine moiety and two terminal dimethylamino groups as illustrated in Scheme 4. The redox function of the quinonediimine moiety is modulated by complexation with the palladium complex **4**, probably due to the stabilization of the generated anionic species. The added electrons are considered to be delocalized over the Pd(II)-quinonediimine d-π* system.

Scheme 4



The similar complexation of the palladium species possessing two coordination sites results in a variety of conjugated complexes with the alternative array of the palladium and ligand units. The structure of the complex depends on the coordination mode of both units. The polymeric palladium(II) complex **7** is formed by treatment of **5** with $PdCl_2(MeCN)_2$ as shown below.[11] Use of the *cis*-palladium(II) complex affords the cyclic 3:3 complex **8** as a cyclic conjugated system. The single-crystal X-ray structure determination of **8** indicates the coordination of both quinonediimine nitrogens to palladium centers in *syn* configuration with the Pd-Pd separation 7.68Å. The quinonediimine planes are inclined in the range of 28° to the plane defined by the six nitrogen atoms of the quinonediimine, creating an open cavity with different faces.



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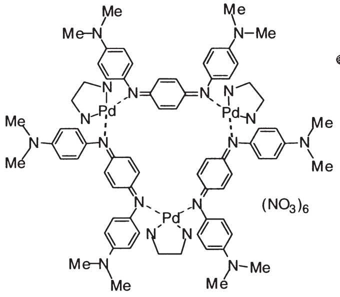
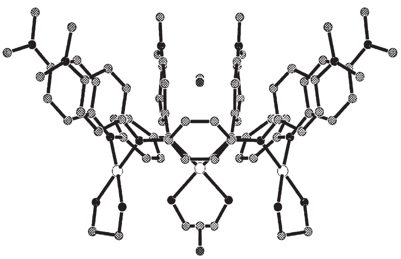


8



Molecular structure of **8**.(Hydrogen atoms and NO_3^- anions are omitted for clarity). Two MeOH molecules are located in above and below the cavity.

Conclusion

A combination of transition metals and π-conjugated redox-active molecules or polymers are considered provides the hybrid multi-redox conjugated complexes via structurally controlled complexation. Electronic communication through d,π-conjugation might be possible in these systems, permitting a potential field reflected by both redox properties. The conjugated complexes are considered to be of importance as functionalized materials and catalysts.[12]

Acknowledgments

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