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Conjugated systems composed of transition metals and redox-active π-conjugated ligands

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Contents

Abstract

A combination of transition metals and π-conjugated molecules or polymers as redox-active ligands leads to the hybrid conjugated complexes. A variety of structural designs are possible based on the coordination number and geometry, affording an efficient multi-redox system. This review focuses mostly on conjugated complexes with *p*-quinone, *p*-quinonediimine, and polyaniline derivatives to give bimetallic, metallocyclic, and polymeric complexes. Complexes with polyanilines are used in the catalytic oxidation reactions, for example, the Wacker oxidation, in which the π-conjugated polymers serve as a redox-active ligand.

Keywords: π-Conjugated molecules; π-Conjugated polymers; Redox-active ligands; Conjugated complexes; Multi-redox systems; Reversible redox cycle

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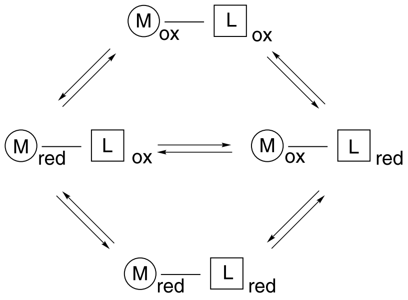
1. Introduction

Efficient transition metal redox processes for electron transfer are essential to develop functionalized materials and catalysts. Ligand coordination is able to control redox processes, so ligand design is one of the key factors to construct an efficient redox system. Furthermore, if the ligands are redox active, a combination of the redox properties of the ligand and the metal is considered to provide a multi-redox system as exemplified by Scheme 1. The redox interaction between transition metals and redox sites of ligands appears to operate through coordination, but if the redox site is not coordinated directly, the interaction is allowed also through bond or through space [1]. A more efficient redox function is likely to be realized in both systems.



Scheme 1. A multi-redox system composed of transition metals and redox-active ligands.

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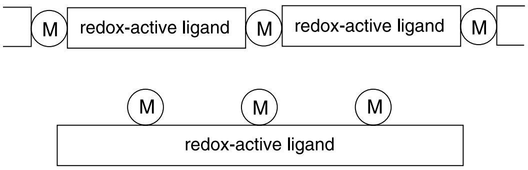
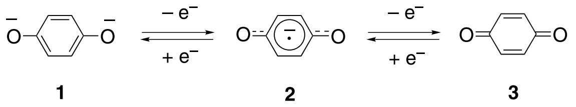
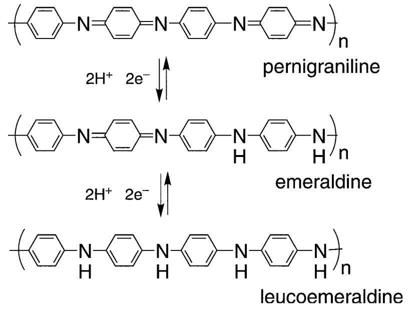


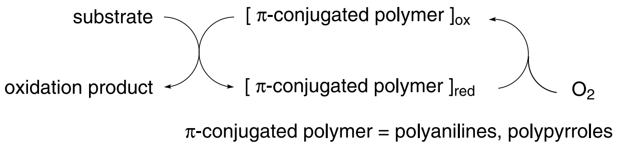
Fig. 1. Design of the multi-redox complexes with redox-active π-conjugated ligands.



Scheme 2. Redox states of *p*-benzoquinone.



Scheme 3. Redox states of polyaniline.



Scheme 4. A catalytic scheme for synthetic metal catalyzed oxidation.

π-Conjugated molecules and polymers, which possess redox-active properties and coordination sites, are allowed to serve as redox-active ligands to afford d,π-conjugated complexes. A characteristic feature of these conjugated complexes is that transition metals can interact with each other through the π-conjugated backbone to permit electronic communication as reported in molecular wire systems [2].

If the π-conjugated ligand possesses more than two coordination sites, at least two systems can be designed as shown in Fig. 1. In the case of both metals and ligands possessing two coordination sites, these components are arrayed alternatively to give the corresponding polymer complexes with linear structure. Depending on their geometries, a cyclic skeleton structure is also possible. Another designed system is derived by multi-coordination with a redox-active π-conjugated ligand, giving a multi-nuclear complex. Based on the number and geometry of the coordination sites, systems with a variety of dimensionally designed structures can be constructed. This review focuses mostly on conjugated systems composed of transition metals and redox-active π-conjugated ligands.

2. Redox-active π-conjugated ligands

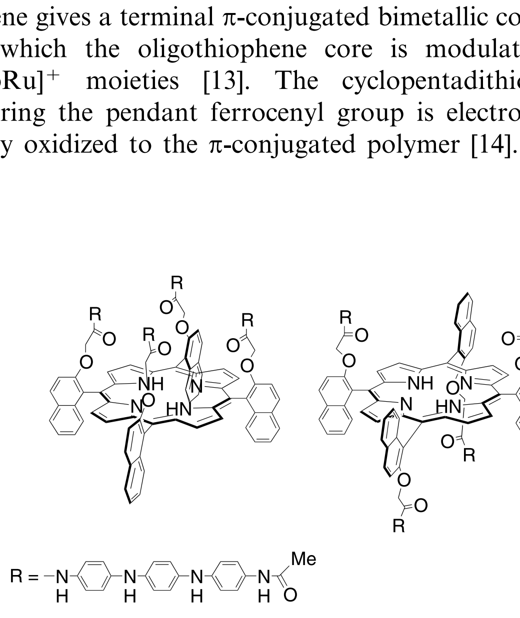
From the viewpoint mentioned above, quinone or quinonediimine derivatives are a candidate unit for redox-active π-conjugated ligands. The former is present in three different redox states: the reduced hydroquinone dianion **1**, the partially reduced semiquinone radical anion **2**, and quinone **3** (Scheme 2). A variety of transition metal complexes with *o*-quinones or their reduced species have been extensively investigated, probably due to their high stability [3]. Furthermore, complexes with quinone ligands have been proposed in catalytic reactions [4]. The redox properties of some palladium(0) complexes with *p*-quinone ligands are known, but only a few high valent complexes with *p*-quinone ligands have been reported [5]. The coordination behavior of simple *p*-benzoquinonediimines has hitherto remained unexplored although 2,5-diamino-1,4-benzoquinonediimine is used as a chelating ligand [6].

π-Conjugated polymers or oligomers have received extensive interest because of their high potential in a variety of applications in electrical materials as conducting compounds. The electronic properties are related to their π-conjugated structure. The π-conjugated polymers or oligomers are also considered to be candidates for a redox-active π-conjugated ligand since π-conjugated moieties are capable of coordinating to transition metals. Furthermore, π-conjugated polymers exist in various redox states as represented by pernigraniline, emeraldine, and leucoemeraldine bases of polyaniline (Scheme 3). Few papers have appeared describing the complexation behavior and redox properties of redox-active π-conjugated polymers.

The oxidation states of the π-conjugated polymers and oligomers interconvert between each other, permitting the construction of a catalytic system for oxidation reactions. Polyanilines and polypyrroles serve as synthetic metal catalysts under an oxygen atmosphere in the dehydrogenative oxidation of benzylamines, 2-phenylglycine, and 2,6-di-*t*-butylphenol (Scheme 4) [7]. Similar catalysis is also achieved with the quinonediimine derivative [8]. The catalytic activity is controlled by protonic acid doping since the presence of a proton source is required for the formation of a reversible redox cycle [9]. Thus, a catalytic system is formed under an oxygen atmosphere.

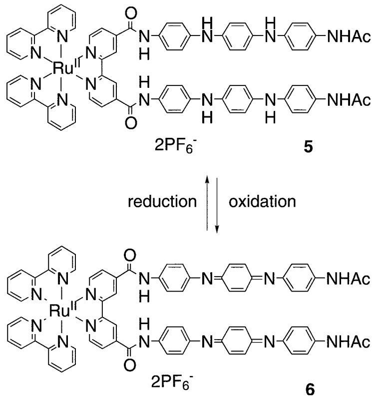
A variety of redox-active π-conjugated ligands are envisaged to be possible based on the design of π-conjugated systems. Extended π-conjugated molecules have been prepared as exemplified by porphrins and porphyrin complexes bearing oligothiophene or polypyrrole substituents at the *meso*-positions [10]. The architecturally ordered orientation and/or assembly of π-conjugated molecular chains are expected to provide three-dimensionally oriented π-electronic systems. The π-conjugated systems **4** (αααα: **4a** and αβαβ: **4b**, Fig. 2) have been constructed by the introduction of four aniline trimer pendant strands to the *meso*-positions of the atropisomeric porphyrin scaffolds, respectively [11]. In the fluorescence emission spectra, the emission from the porphyrin moiety is almost completely quenched in both atropisomers.

The ruthenium(II) complex **5** bearing the *N*,*N*′-bis(4-aminophenyl)-1,4-phenylenediamine moieties was synthesized and chemically oxidized to complex **6** bearing the *N*,*N*′-bis(4-aminophenyl)-1,4-benzoquinonediimine moieties (Scheme 5) [12]. An efficient photoinduced intramolecular electron transfer is also observed with **5**. The linkage of ruthenium π-complexes to oligothiophene gives a terminal π-conjugated bimetallic complex, in which the oligothiophene core is modulated via $[CpRu]^+$ moieties [13]. The cyclopentadithiophene bearing the pendant ferrocenyl group is electrochemically oxidized to the π-conjugated polymer [14].



4a: αααα isomer **4b**: αβαβ isomer

Fig. 2. Three-dimensionally oriented π-conjugated systems **4**.



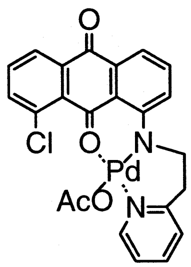
Scheme 5. Ruthenium complexes bearing redox-active π-conjugated pendant moieties.

3. Complexes with redox-active π-conjugated molecules

The coordination of the redox-active anthraquinone ligands **7a** bearing the *N*-heterocyclic coordination site to divalent palladium affords the corresponding 1:1 quinone complex **8a** [15]. The quinone oxygen, which is coordinated to palladium substituted by the amide nitrogen in a position *trans* to the pyridyl nitrogen, is bent out of the anthraquinone plane (Fig. 3). A terminal bimetallic complex possessing this quinone spacer can be formed by the introduction of two *N*-heterocyclic coordination sites. The binuclear palladium(II) complex **8b** is obtained with 1,5-bis{2-(2-pyridyl)ethylamino}-9,10-anthraquinone (**7b**) (Fig. 4). Two palladium atoms of **8b** are revealed to be disposed on opposite faces of the anthraquinone plane, which are arranged in an edge-to-face orientation in the crystal packing. The d,π-conjugated system may interconnect through a π–π interaction between the π-conjugated moieties in the solid state. The cyclic voltammograms of these quinone oxygen-coordinated palladium(II) complexes **8** show two redox couples assignable to the quinone moiety, which are positively shifted by quinone coordination.

Complexation with quinonediimines does not require a pendant coordination site. Treatment of the π-conjugated molecule, *N*,*N*′-bis(4-dimethylaminophenyl)-1,4-benzoquinonediimine (**9**) [16], with the palladium(II) complex **10** bearing *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide [17] yields the 1:2 conjugated palladium(II) complex **11** [18]. Two palladium complex units are bridged by the quinonediimine moiety. The X-ray crystal structure of the isolated C_2-symmetrical complex **11*anti*** reveals that the bridging π-conjugated spacer moieties in *anti* configuration are aligned along a straight line almost parallel to the *a*-axis, to form columns of the π-conjugated molecules (Fig. 5). The conjugated complex **11** exhibits three separate redox waves assignable to the successive one-electron reduction processes of the quinonediimine moiety and the two terminal dimethylamino groups (Fig. 6). In contrast to the quinone ligand **7**, the redox function of the quinonediimine moiety of **9** is modulated by complexation with the palladium complex **10**, probably due to the stabilization of the generated anionic species. The added electrons are delocalized over the Pd(II)–quinonediimine d–π* system. This observation is related to the effect of protonic acid doping in the redox process of **9**. The general scheme for the redox processes of the quinonediimine complex is illustrated in Scheme 6.

Use of the palladium species possessing two coordination sites leads to an alternative coordination array of the palladium and ligand units. The structure of the complexes depends on the geometry of both units [19]. The polymeric palladium(II) complex **12** is formed as



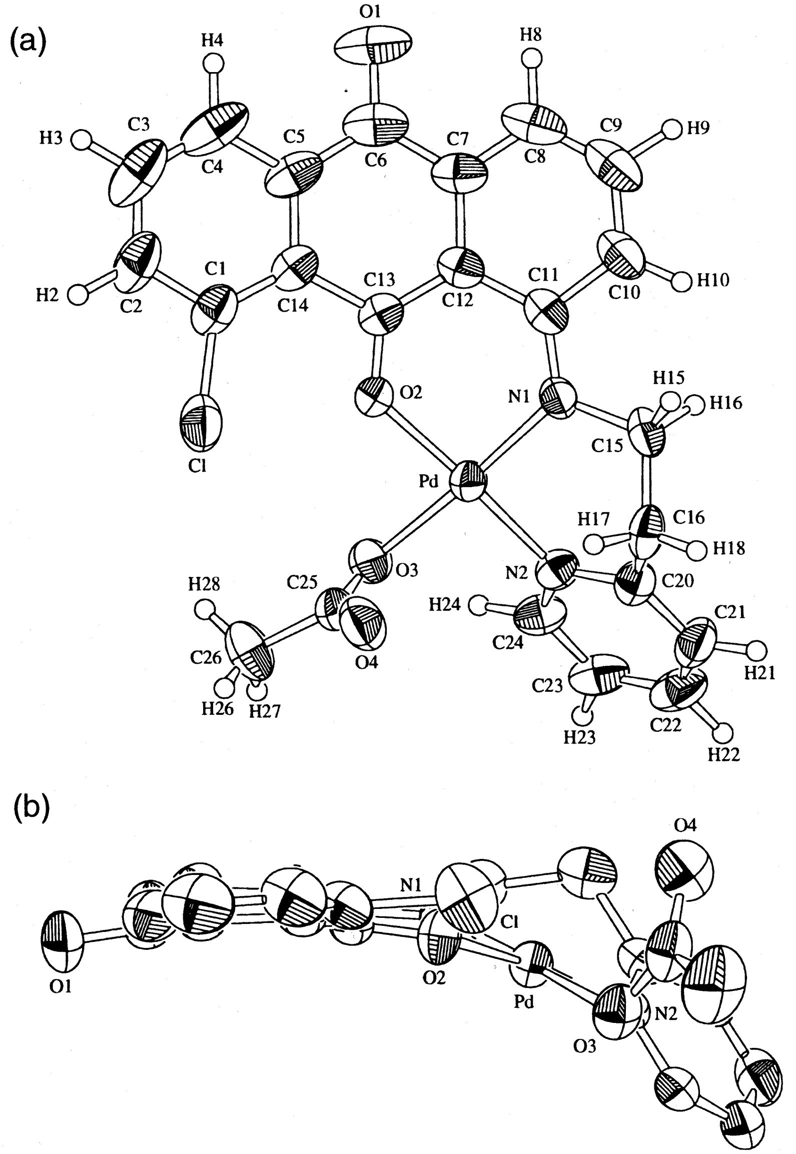
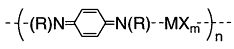


Fig. 3. The X-ray crystal structure of **8a**: (a) top view and (b) side view (40% probability ellipsoids, hydrogen atoms are omitted for clarity).

shown below. Complexation of the *cis*-palladium(II) complex results in the formation of the cyclic 3:3 complex **13**, giving the cyclic conjugated system (Fig. 7). The single-crystal X-ray structure determination of **13** indicates the coordination of both quinonediimine nitrogen atoms to palladium centers in *syn* configuration with the Pd–Pd separation 7.68 Å. 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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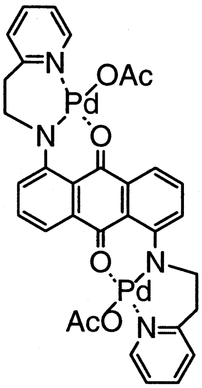
The terthienyl ligand of the ruthenium complex **14** shown in Scheme 7 is recognized as a redox-switchable hemilabile ligand [20].

4. Complexes with redox-active π-conjugated polymers

Complexation of transition metals to a π-conjugated organic ligand possessing relevant redox functions provides a potentially important redox system as described above. π-Conjugated polymers have multi-coordination



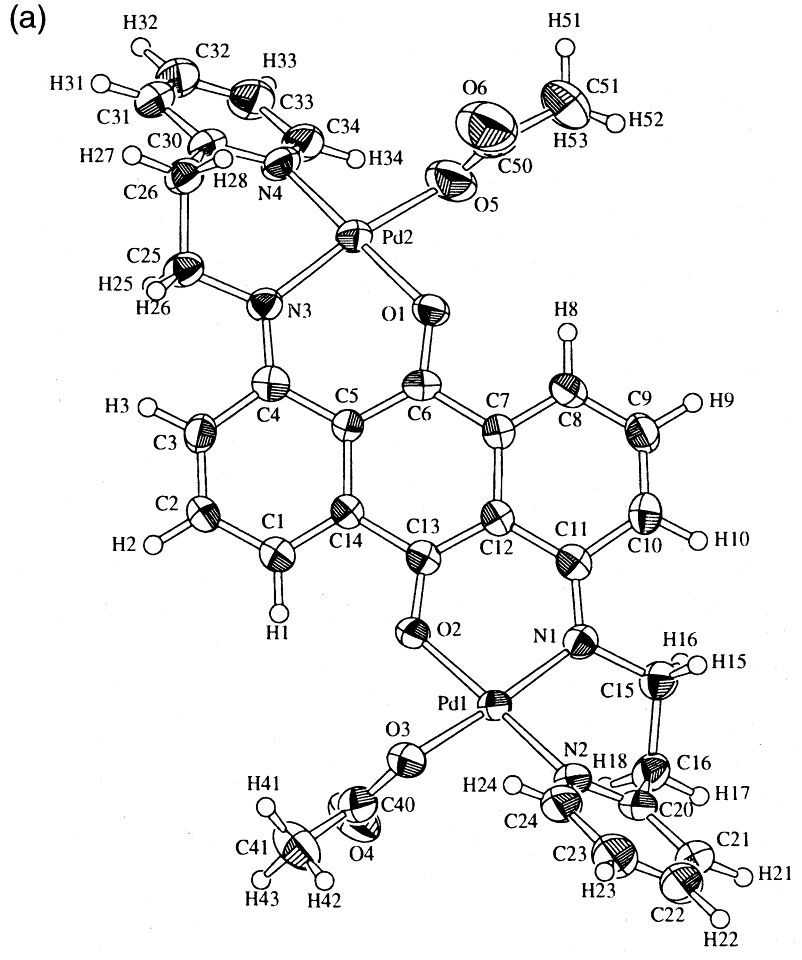


Fig. 4. (a) The X-ray crystal structure of **8b**: (b) top view and (c) side view of the crystal packing diagram (40% probability ellipsoids, hydrogen atoms are omitted for clarity).

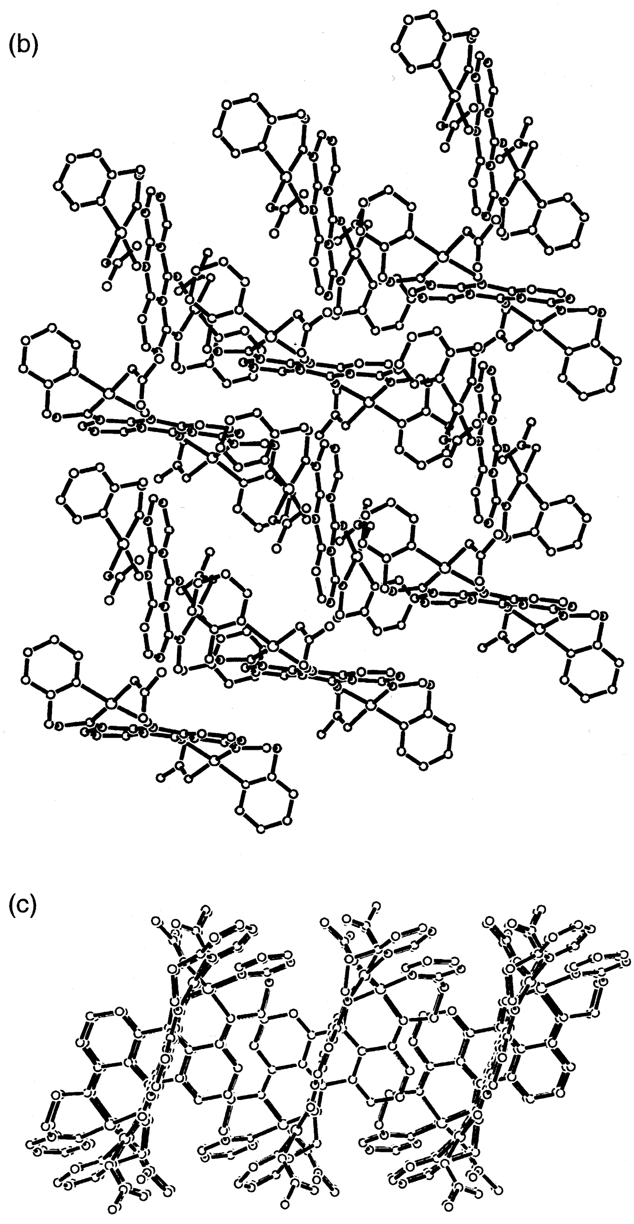
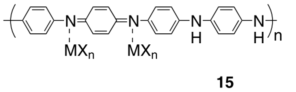


Fig. 4. (*Continued*)

sites to give multi-nuclear complexes as shown in Fig. 1. In the case of polyanilines, the quinonediimine moieties of the emeraldine base participate in coordination with the formation of **15**. Electronic communication is considered to be permitted between metals through a π-conjugated backbone chain.



$$\left[C_6H_4-\underset{\vdots \atop MX_n}{N}=C_6H_4=\underset{\vdots \atop MX_n}{N}-C_6H_4-\underset{H}{N}-C_6H_4-\underset{H}{N} \right]_n$$

15

The Cu(II) complex with polyaniline exhibits a higher catalytic capability for the dehydrogenation of cinnamyl alcohol into cinnamaldehyde [7]. The cooperative catalysis of polyaniline and copper(II) chloride is essential. Iron(III) chloride is similarly used instead of copper(II) chloride. The catalytic system is applicable to the decarboxylative dehydrogenation of mandelic acid to produce benzaldehyde. In these oxidation reactions, a complex catalyst consisting of polyaniline and metal salt forms a reversible redox cycle under an oxygen atmosphere as shown in Scheme 8. The complexation behavior with Cu(II) salt is monitored spectroscopically. Treatment of the undoped polyaniline (anal. $C_{6.00}H_{4.04}N_{0.97}Cl_{0.03}$) with copper(II) chloride in 1-methyl-2-pyrrolidinone (NMP) leads to the appearance of a new absorption band in the shorter wavelength region, as compared with the absorption around 640 nm, attributable to charge transfer from the benzenoid of polyaniline to the quinoid in the UV–vis spectra [21]. The copper salt plays an important role to serve as a similar dopant as observed in the protonic acid doping. The reduced phenylenediamine anionic species is stabilized by complexation.

The redox interaction between metals and redox-active ligands largely contributes to a smooth reversible redox cycle of transition metal catalyzed oxidation reactions. Actually, the Wacker oxidation reaction of a terminal olefin proceeds catalytically to give 2-alkanone only in the presence of a catalytic amount of polyaniline derivative as a cocatalyst in acetonitrile–water under an oxygen atmosphere (Scheme 9) [22]. Catalysis is not observed in the absence of the polyaniline derivative, indicating that the π-conjugated polymer participates in the catalytic cycle of a palladium species. Polypyrroles can be employed similarly [23]. A difference in the electronic state of the polymer affects the catalysis. A real catalyst is formed by complexation of a palladium species with the π-conjugated polymer. The polyaniline redox process can be monitored by UV–vis spectra. A new broad absorption around 635 nm appears upon treatment of poly(*o*-anisidine) with $Pd(OAc)_2$ in NMP and is probably attributable to a palladium complex formed with poly(*o*-anisidine). This broad absorption disappears in the reaction with 1-decene and water under an argon atmosphere. Bubbling oxygen through this solution gives rise to the broad absorption around 600 nm with isosbestic points. A similar spectrum is obtained by bubbling oxygen through the solution of $Pd(OAc)_2$ and poly(*o*-anisidine). These results support the view that π-conjugated polymers behave as redox-active ligands based on their reversible redox function in transition metal catalyzed oxidation reactions under an oxygen atmosphere [24]. The solubility of the complex catalysts depends on the substituent on the polymer, which allows one to provide both homogeneous and heterogeneous catalytic systems.

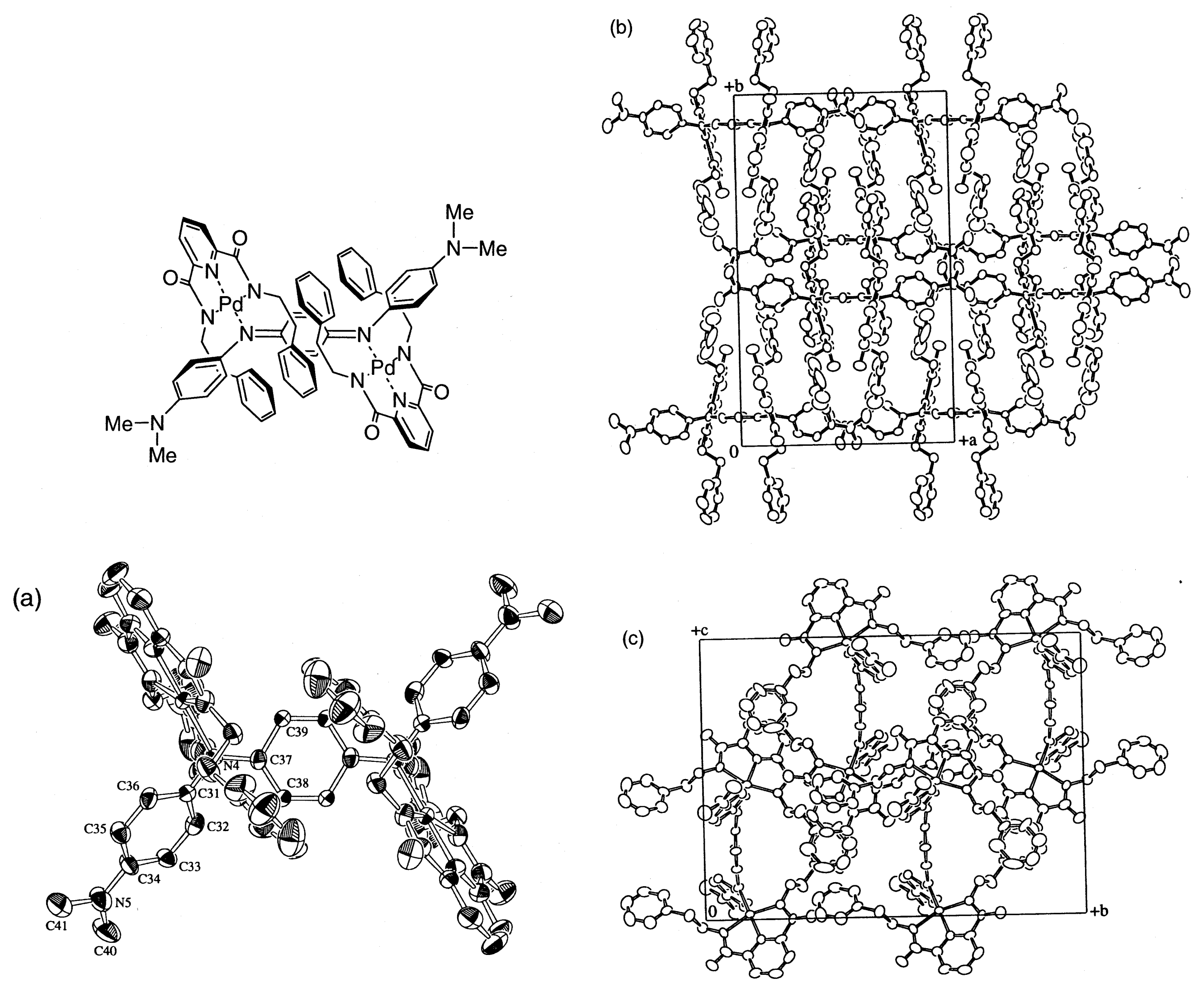


Fig. 5. (a) The X-ray crystal structure of **11*anti*** (40% probability ellipsoids, hydrogen atoms are omitted for clarity). (b) Top view is a projection down the *c*-axis. (c) Bottom view is a projection down the *a*-axis of the molecular packing of **11*anti***.

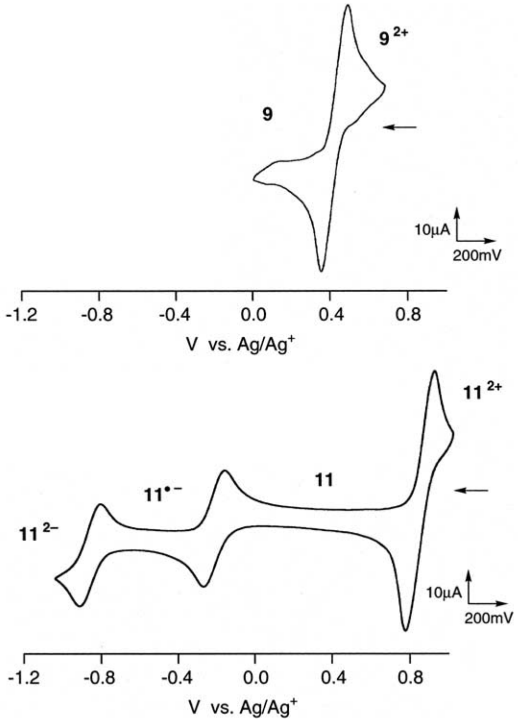
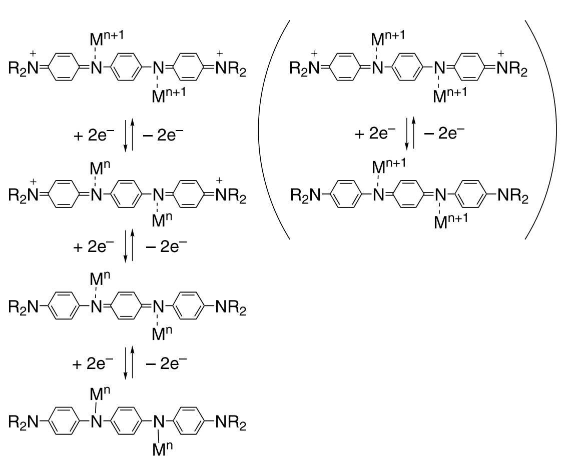


Fig. 6. Cyclic voltammograms of **9** and **11** (1.0×10^{-3} M) in dichloromethane (0.1 M Bu_4NClO_4) as a glassy carbon working electrode with scan rate = 100 mV s^{-1} under an argon atmosphere.



Scheme 6. Redox processes of the quinonediimine complex.

The controlled complexation of the polyaniline derivative is performed in organic solvents to afford the structurally defined conjugated complexes [25]. The spectral measurement supports the formation of such a polymer complex. On treatment of the emeraldine base of poly(*o*-toluidine) possessing the amine and imine moieties at ca. 1:1 ratio in THF with $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$, a new absorption band appears in the longer wavelength region when compared with the CT band of the polymer around 590 nm. The titration experiment shows the formation of the ca. 4:1 complex of the *o*-toluidine and palladium units. Although a similar red shift to 710 nm is observed in complexation with **10**, the ratio is then ca. 2:1. The ratio difference is explained as follows. Two coordination sites can be

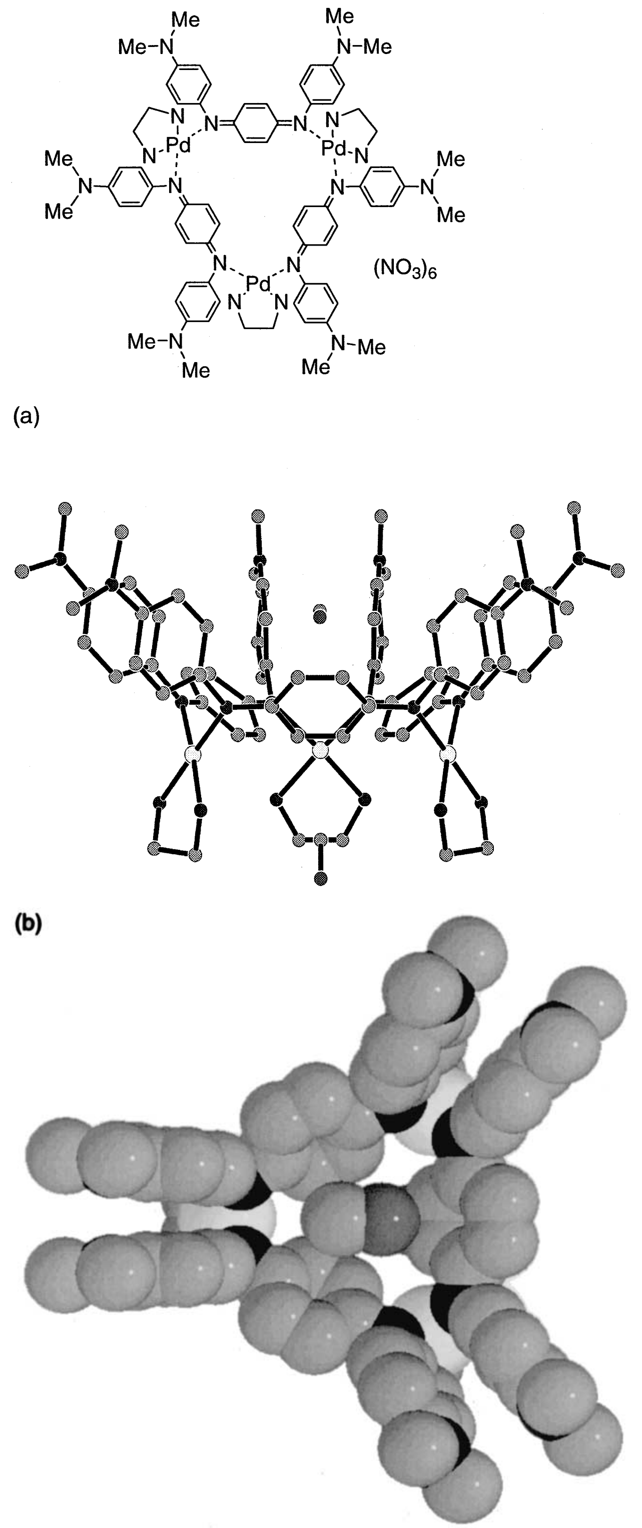
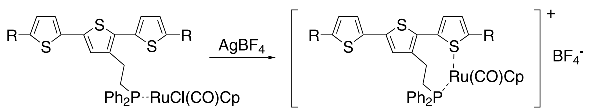


Fig. 7. The cyclic 3:3 palladium complex **13**: (a) Molecular structure of **13** (hydrogen atoms and NO_3^- anions are omitted for clarity). Two MeOH molecules are located above and below the cavity. (b) Space-filling representation of the molecular structure of **13** (hydrogen atoms and NO_3^- anions are omitted for clarity).



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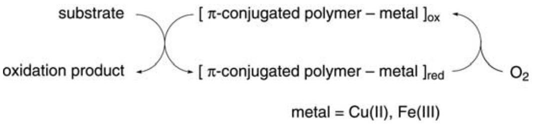
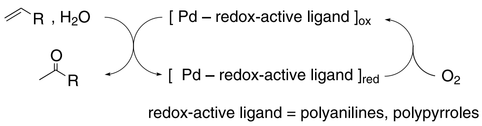
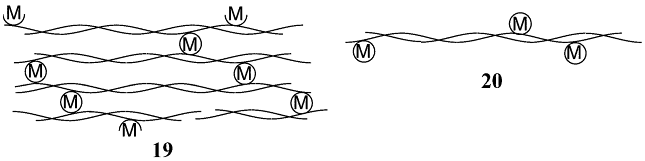
Scheme 7. The ruthenium complex **14** with the terthienyl ligand.



Scheme 8. A catalytic scheme for π-conjugated complex induced oxidation.

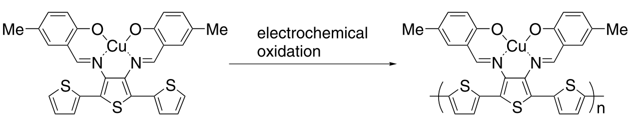


Scheme 9. A catalytic scheme for the palladium-catalyzed oxidation in the presence of a redox-active ligand.



19 **20**

Fig. 8. Conjugated network system **19** and conjugated single-strand system **20**.



22 **23**

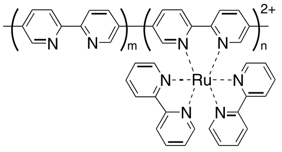
Scheme 10. The salen complex **23** with polythiophene backbone.

used for complexation in the case of $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$, in contrast to only one coordination site available for complex **10** bearing the tridentate ligand. The quinonediimine moieties of the emeraldine polymer are capable of participating in the complexation, possibly affording a cross-linked synthetic metal–transition metal conjugated network system **19** in the former case as shown in Fig. 8. On the contrary, a conjugated single-strand system **20** is considered to be formed in the latter case.

Heterobimetallic complexes are of potential in redox reactions and materials based on intermetallic interactions of different metals through a π-conjugated spacer. A heterobimetallic complex has been prepared, for example, by successive treatment of poly(*o*-toluidine) with $Cu(OAc)_2$ and $Pd(OAc)_2$ [26].

The emeraldine base of poly(*o*-toluidine) or *N*,*N*′-bis(4′-dimethylaminophenyl)-1,4-quinonediimine (**9**) undergoes oxidative complexation with VCl_3, affording the corresponding conjugated complexes [27]. In this process, the CT band between the benzenoid and quinoid moieties disappears, consistent with the reduction of the quinonediimine moiety. The complexation proceeds via reduction of the quinonediimine moieties along with oxidation of V(III) to V(IV), in which the vanadium species serves both as a metallic dopant and as a one-electron reductant.

The incorporation of ruthenium centers in the polymer backbone yields the bipyridine ruthenium complexes **21** [28]. These conjugated ruthenium bipyridine complexes are photorefractive materials. Other transition metals form corresponding complexes [29]. The pyridine unit could be replaced by bithienyl, 1,4-diazabutadiene, ethylene, benzimidazole, or thiazole [30].



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A salen complex is incorporated to a polythiophene backbone by anodic polymerization of the terthiophene derivative **22** (Scheme 10) [31].

5. Conclusions

Conjugated complexes composed of redox-active π-conjugated molecules or polymers, transition metals and provide novel multi-redox systems. Electronic communication between metals might be possible in these systems, permitting the potential field reflected by both redox properties. These systems have promise for the development of efficient catalysts and materials in the future.

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This work was mostly done by Dr Moriuchi and the students in our laboratory, whose names are cited in the references.

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