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Design and Redox Function of Conjugated Complexes with Polyanilines or Quinonediimines

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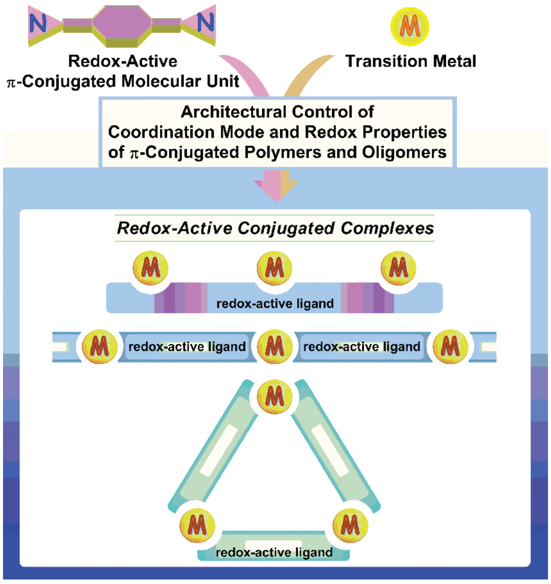

Because of their potential application as new electrical materials that depend on their redox properties, π-conjugated polymers and oligomers have attracted much attention. Polyanilines, which are chemically stable, are one of the promising classes of conducting π-conjugated polymers. Polyanilines exist in three different discrete redox forms, which include the fully reduced leucoemeraldine, the semioxidized emeraldine, and the fully oxidized pernigraniline base form. The redox-active 1,4-phenylenediamine (PD) and 1,4-benzoquinonediimine, unit molecules of the emeraldine base form, can bind to transition metals to afford novel conjugated complexes. The introduction of metal centers into π-conjugated polymers is expected to dramatically change their functions.

In this Account, we describe our ongoing research into the construction of conjugated complexes with redox-active π-conjugated polyanilines and 1,4-benzoquinonediimines. These systems can form architecturally controlled functionalized systems that depend on their dynamic redox properties, resulting in highly selective and versatile electron-transfer reactions and functionalized materials.

Complexation with metals (Pd, V, Cu, etc.) occurred via the two nitrogen atoms of the quinonediimine moiety of the emeraldine base form of poly(*o*-toluidine) to afford the single-strand or cross-linked network conjugated complexes with d,π-conjugation. The complexation of the redox-active π-conjugated 1,4-benzoquinonediimines, unit molecules of the emeraldine base form, with palladium(II) compounds yielded a variety of conjugated complexes. Through regulation of the coordination mode of the quinonediimine moiety, we were able to architecturally control the formation of conjugated bimetallic, polymeric, or macrocyclic complexes.

Complexation modulated the redox function of the quinonediimine moiety. Introduced metals act as a metallic dopant, and the complexed quinonediimine is stabilized as an electron sink. Furthermore, chirality could be induced into a π-conjugated backbone through complexation with optically active transition compounds, resulting in chiral d,π-conjugated complexes. We could also modulate the functional properties of conjugated complexes based on the redox states of the redox-active π-conjugated moieties.

We also demonstrated how complexes with redox-active π-conjugated molecules can control the architecture of redox-functionalized systems through the metal imido bonds of these systems. Using the one-pot preparation of (arylimido)vanadium(V) compounds from the corresponding anilines, we synthesized binuclear complexes with axial chirality and trinuclear complexes with a tridendritic centrosymmetric structural motif. Such structures showed a strong tendency to self-assemble.

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Introduction

The construction of efficient redox processes of transition metal complexes is essential to develop functionalized materials and catalysts.[1] Coordination interactions of ligands are able to control the redox processes; therefore ligand design is one of the key factors for efficient redox systems. Furthermore, if ligands are redox active, the combination of both redox properties of the transition metals and ligands is considered to provide multiredox systems. The organic bridging ligand provides electronic communication between the redox sites.

π-Conjugated polymers and oligomers have attracted much attention for the application of electrical materials depending on their redox properties.[2] The function of π-conjugated polymers is envisioned to be modified dramatically by introduction of metal centers into the polymers.[1d,f,3] π-Conjugated polymers and molecules, which possess redox-active properties and coordination sites, are allowed to serve as redox-active ligands to afford the d,π-conjugated complexes. If the π-conjugated ligand possesses more than two coordination sites, two systems with different structures can be designed basically as shown in Figure 1. In the case of both metals and ligands possessing two coordination sites, these components are arrayed alternatively to give the corresponding polymer complexes. One possible application for these complexes is as materials for molecular wires.[4] Depending on their coordination geometries, a cyclic skeleton structure is also allowed to be formed. Another designed system is derived by multicoordination with a redox-active π-conjugated ligand, giving the multinuclear complex. Based on the number and geometry of the coordination sites, the systems with a variety of dimensionally designed structures can be constructed.

Polyanilines are promising conducting π-conjugated polymers with chemical stability. Polyanilines exist in three different discrete redox forms, which include the fully reduced leucoemeraldine, the semioxidized emeraldine, and the fully oxidized pernigraniline base form.[2a] The quinonediimine (QD), which is an oxidized molecular unit of polyanilines and possesses binding sites to metals, is reduced to a semiquinonediimine radical anion (SQ) and a phenylenediamine dianion (PDA). The combination of this redox behavior and complexation with transition metals is expected to provide efficient redox systems. In this context, a variety of transition metal complexes with 1,2-benzoquinonediimines or their reduced species have been investigated extensively.[5] However, only few studies on transition metal complexes with 1,4-benzoquinonediimines have been reported, and the coordination behavior of 1,4-benzoquinonediimines has hitherto remained unexplored.[6]

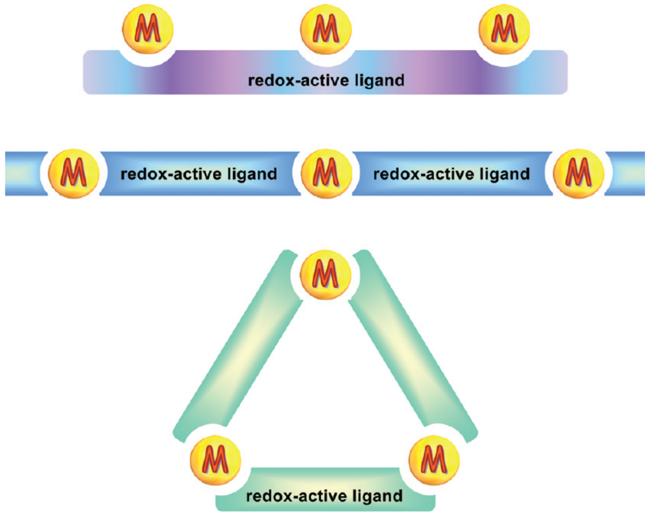


FIGURE 1. Design of conjugated complexes with redox-active π-conjugated ligands.

In this Account, we summarize our ongoing research into the design of the conjugated complexes with redox-active π-conjugated polyanilines and 1,4-benzoquinonediimines for an architecturally controlled formation of conjugated complexes. The functional properties based on the redox states of the π-conjugated bridging spacer are also addressed.

Architecturally Controlled Formation of Conjugated Complexes with Polyanilines or 1,4-Benzoquinonediimines

The controlled complexation of the emeraldine base of poly(*o*-toluidine) (POT) with palladium(II) compounds was performed in an organic solvent to afford conjugated polymer complexes.[7] Two nitrogen atoms of the quinonediimine (QD) moieties were found to be available for complexation in the case of $Pd(OAc)_2$ and $PdCl_2(MeCN)_2$, which have two coordination sites, affording cross-linked conjugated complexes **1** under nanospace control (Figure 2). In contrast, only one coordination site was used with the palladium(II) complex **2**[8] bearing the tridentate ligand (L^1H_2),[9] in which a conjugated single-strand complex **3** is likely to be formed. Poly(3-heptylpyrrole) served as an efficient π-conjugated ligand to afford a similar conjugated complex with $PdCl_2(MeCN)_2$. An organic light-emitting diode device with the thus-obtained conjugated complex film as a hole injection layer revealed maximum luminance of 11 000 cd/m^2 at 10 V, which was 2 V lower than a device with the conventional copper phthalocyanine (CuPc) hole injection layer.[10] The conjugated complexes with π-conjugated polymers like

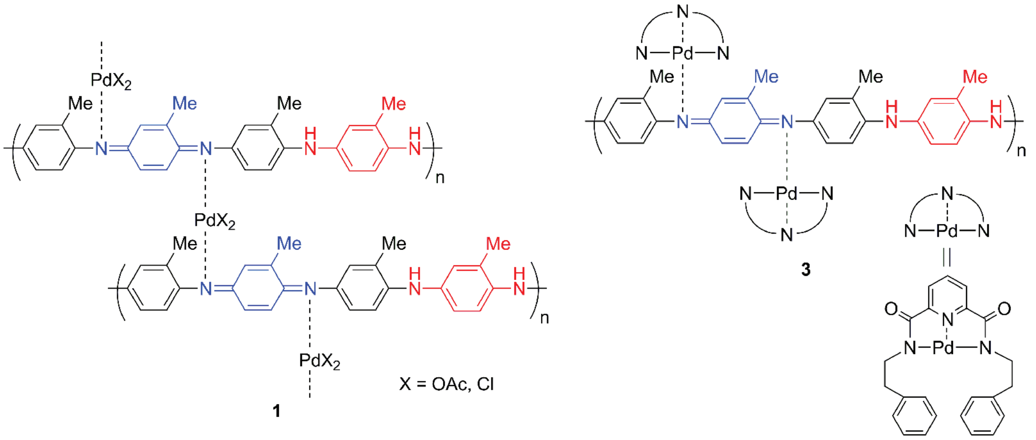
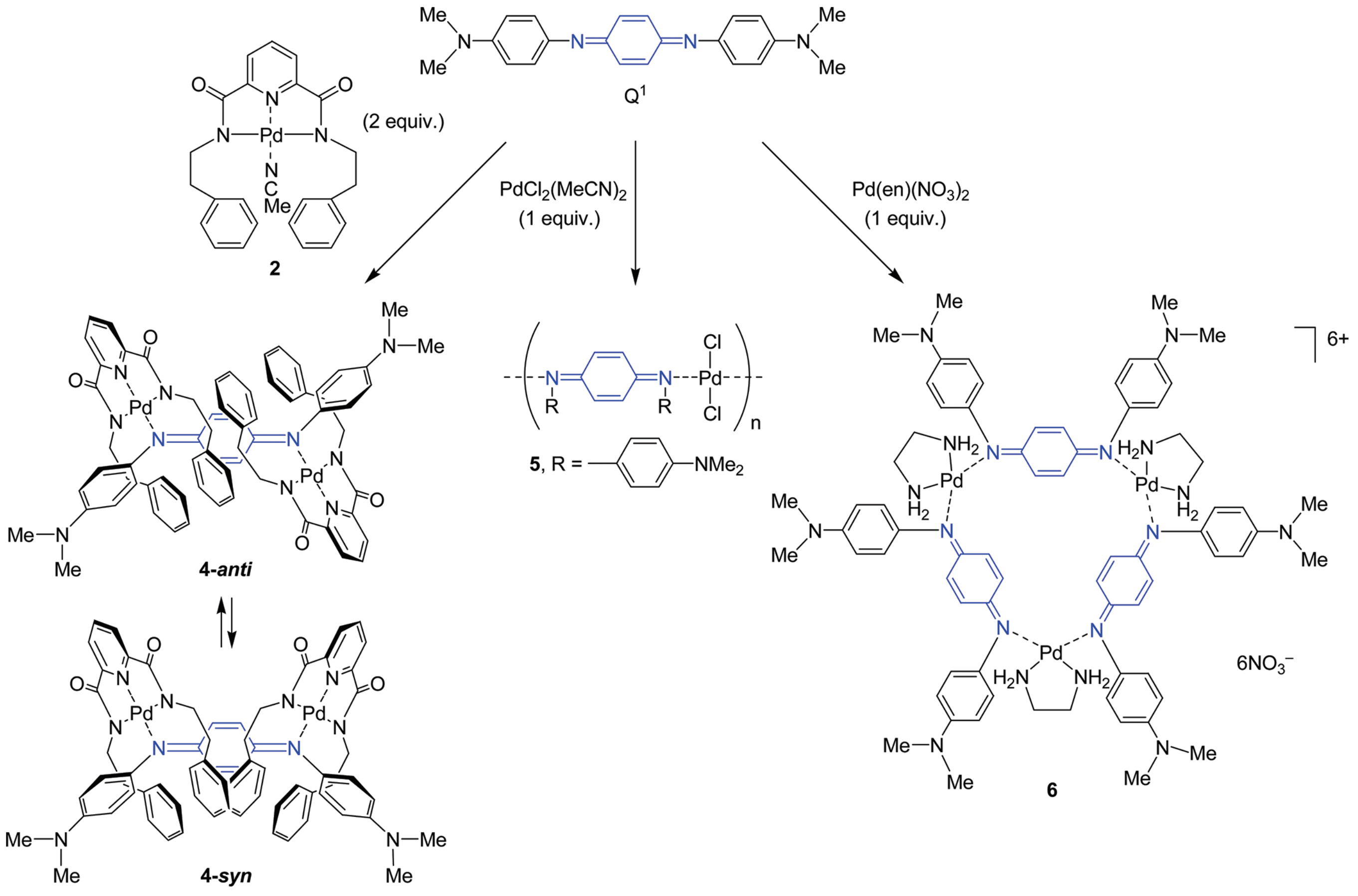


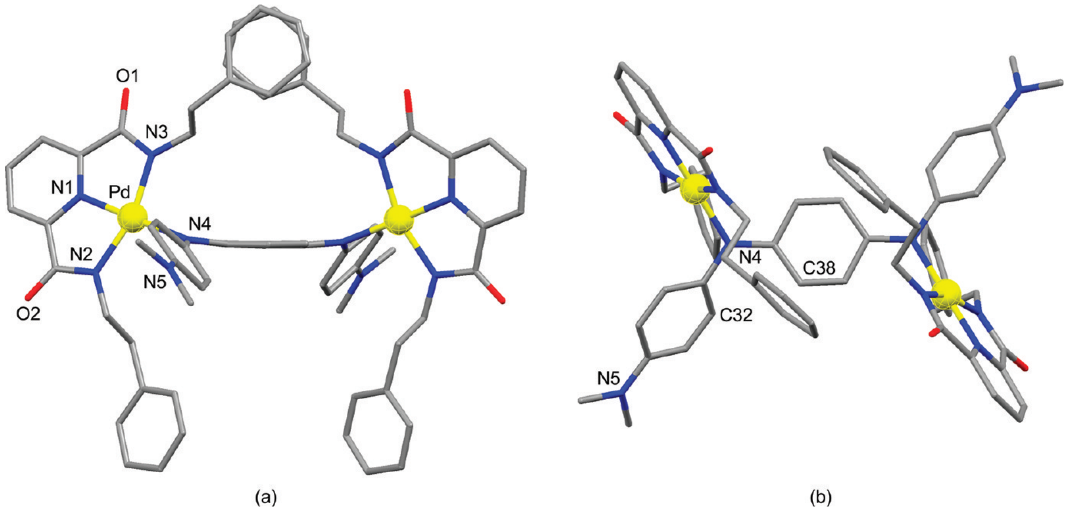
FIGURE 2. (a) A cross-linked network of conjugated complexes **1** and (b) a single-strand conjugated complex **3**.

SCHEME 1. Controlled Formation of **4**, **5**, or **6** with Q^1



polyanilines or polypyrroles have been demonstrated to afford redox systems depending on their complex structures and redox properties. For example, copper salts could be employed in the formation of the reversible redox cycle of undoped polyanilines.[11] The polymer complex could effectively serve as an oxidation catalyst,[12] in which the QD moiety is considered to contribute to a reversible catalytic redox process of a transition metal. The catalytic Wacker reaction was allowed to proceed with polymer complexes under molecular oxygen.[12b,c]

To gain further insight into the coordination properties and structures in the complexation with the QD moieties, the complexation behavior of a redox-active π-conjugated molecule, *N*,*N*′-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine (Q^1)[13] was investigated as a model molecule



(a) (b)

FIGURE 3. (a) A top view and (b) a side view of the molecular structure of ***4-anti*** (hydrogen atoms are omitted for clarity).

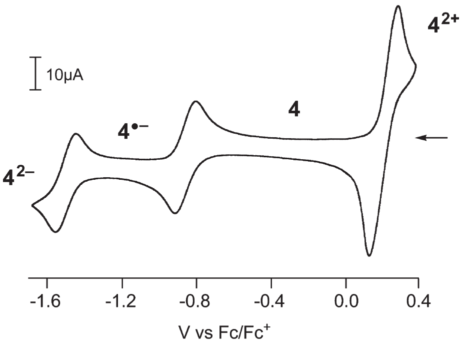


FIGURE 4. Cyclic voltammogram of **4** (1.0×10^{-3} M) in dichloromethane (0.1 M $n\mathrm{Bu_4NClO_4}$) at a glassy carbon working electrode with scan rate = 100 mV/s under Ar.

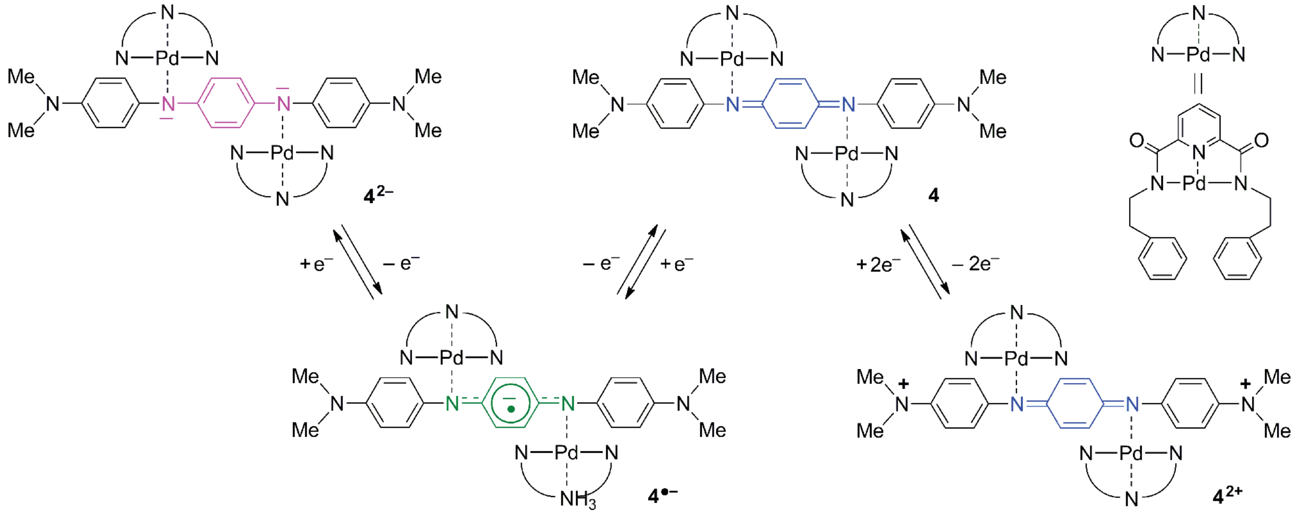
of polyaniline. The complexation of Q^1 with two equimolar amounts of the palladium(II) complex **2** led to the formation of the 1:2 conjugated homobimetallic palladium(II) complex $[(L^1)Pd(Q^1)Pd(L^1)]$ (**4**, Scheme 1).[14] The crystal structure of ***4-anti*** showed that the two $[(L^1)Pd]$ units are bridged by the QD moiety of Q^1 as depicted in Figure 3. Each phenylene ring of Q^1 has an opposite dihedral angle with respect to the QD plane, causing a propeller twist of 79.8° between the planes of the two phenylene rings.

The conjugated complex **4** in dichloromethane showed three separate redox waves ($E_{1/2} = -1.49$, -0.85, and 0.20 V vs Fc/Fc^+) (Figure 4). The waves at -1.49 and -0.85 V are assigned to the successive one-electron reduction of the QD moiety to give the corresponding reduced species. This result is in sharp contrast to the redox behavior of Q^1 in dichloromethane, in which an irreversible reduction wave was observed at -1.67 V. Generally, the generated radical anion appears to be unstable, although this depends on the availability of a proton source.[15] The most positive anodic peak with twice the current ($E_{1/2} = 0.20$ V) is attributable to one-electron oxidation process of the two terminal dimethylamino groups. A substantial positive shift of this oxidation wave compared with the free QD Q^1 ($E_{1/2} = -0.08$ V) is consistent with the coordination of Q^1 to palladium. Redox behavior of the conjugated complex **4** is schematically depicted in Scheme 2. The ESR measurement indicates that the unpaired electron is located mostly on the QD moiety although delocalization to some extent onto the metal was revealed by the weak satellite lines due to ^{105}Pd coupling. In the case of the reduction of the complex **4**, the added electrons are considered to be delocalized over the $Pd^{II}-QD$ $d-\pi^*$ system. Compared with the uncomplexed form, the complexed QD is stabilized as an electron sink. Accordingly, the redox properties of the QD moiety were found to be modulated by complexation with the palladium complex **2**, affording a multiredox system.

On the other hand, complexation of Q^1 with $[PdCl_2(MeCN)_2]$ having two coordination sites in acetonitrile gave the conjugated polymeric complex **5**, in which palladium centers are introduced in the main chain (Scheme 1).[16] In the conjugated polymeric complex **5**, both *syn* and *anti* isomers of the QD moieties are likely to be present.

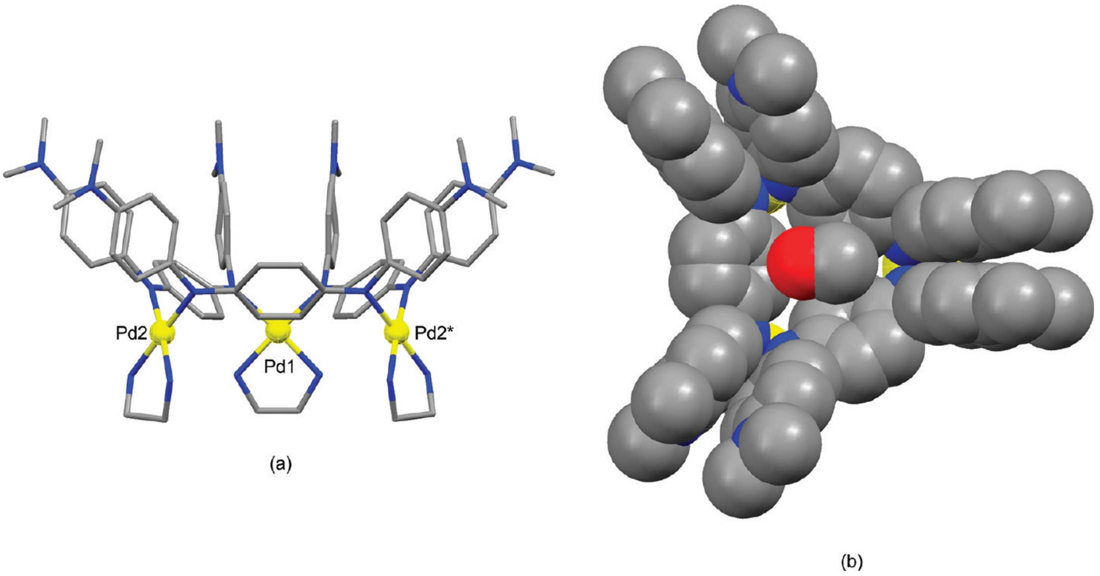
To regulate the coordination mode of the QD moiety, a metal-directed assembly for the construction of metallomacrocycles was embarked upon by using $[Pd(NO_3)_2(en)]$, which has *cis* binding sites as a "metal clip". The conjugated trinuclear macrocycle $[\{Pd(en)(Q^1)\}_3](NO_3)_6$ (**6**) was obtained quantitatively by treating Q^1 with an equimolar amount of $[Pd(NO_3)_2(en)]$ (Scheme 1).[16] The crystal structure of **6** confirmed a trimetallic macrocyclic skelton and the coordination of both QD nitrogen atoms to the palladium centers in the *syn*

SCHEME 2. Schematic Representation of the Redox Behavior of **4**



configuration (Figure 5). The noteworthy structural feature is the orientation of the phenylene rings of Q^1 in a face-to-face arrangement at a distance of about 3.5 Å at each corner of the triangle, which indicates a $\pi-\pi$ stacking interaction (Figure 6). An open cavity possessing different faces was formed with the cone conformation. This inclination of the QD planes is probably due to the coordination of the nitrogen atoms to the palladium centers. The macrocycle **6** accommodated two methanol molecules at the top and bottom of the cavity. A preliminary experiment on guest binding in D_2O showed that the association constant for 1,2-dimethoxybenzene, calculated from ^{1}H NMR spectroscopic data, was 4.0×10^3 M^{-1}.

In recent years, there has been an increased interest in chiral induction of polyanilines because of their potential use in diverse areas such as surface modified electrodes, molecular recognition, and chiral separation.[17] Chiral polyanilines are formed by chiral acid dopants.[17] Complexation with optically active transition metal compounds induces chirality to a π-conjugated backbone of polyanilines, giving the corresponding chiral d,π-conjugated complexes. The chiral conjugated polymer complex [POT−((*S*,*S*)-L^2Pd)] ((*S*,*S*)-**8**) was obtained by the reaction of the emeraldine base form of POT with the chiral palladium(II) complex [((*S*,*S*)-L^2)Pd(MeCN)] ((*S*,*S*)-**7**) (Scheme 3).[18] The UV−vis spectrum of (*S*,*S*)-**8** showed



(a)
(b)

FIGURE 5. (a) The molecular structure of **6** (hydrogen atoms and NO_3^- ions are omitted for clarity). (b) Space-filling representation of the molecular structure of **6** (hydrogen atoms and NO_3^- ions are omitted for clarity). Two methanol molecules are located at the top and bottom of the cavity.

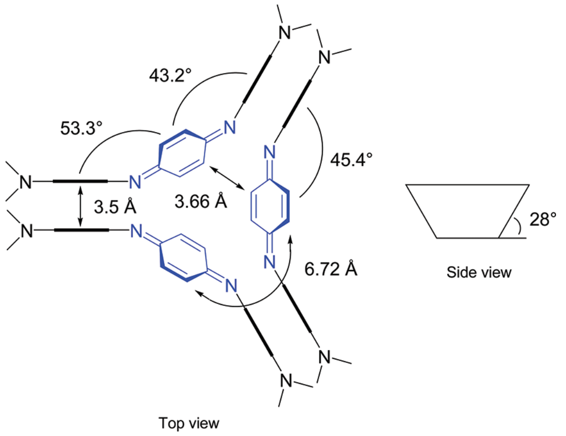


FIGURE 6. Schematic representation of **6**.

a broad absorption around 500−900 nm, which is probably due to a low-energy charge-transfer transition with significant contribution from palladium (Figure 7). Furthermore, the mirror image relationship of the ICD signal around 500−850 nm was observed with (*R*,*R*)-**8** (Figure 7), supporting the chirality induction in the case of POT. The random twist conformation of POT might be transformed into the helical conformation with a predominant screw sense through complexation.

To gain further insight into the chirality induction of π-conjugated backbones, the chiral complexation behavior of Q^1 was investigated. Complexation of Q^1 with two equimolar amounts of chiral palladium(II) complex (*S*,*S*)-**7** or (*R*,*R*)-**7** afforded the chiral 1:2 conjugated homobimetallic palladium(II) complex [((*S*,*S*)-L^2)Pd(Q^1)Pd((*S*,*S*)-L^2)] ((*S*,*S*)-**9**) or [((*R*,*R*)-L^2)Pd(Q^1)Pd((*R*,*R*)-L^2)] ((*R*,*R*)-**9**), respectively (Scheme 3).[18] The mirror image relationship of the CD signals around a low-energy charge-transfer transition with significant contribution from palladium (600−900 nm) of the QD moiety was observed between (*S*,*S*)-**9** and (*R*,*R*)-**9** in dichloromethane as shown in Figure 8. Such induced circular dichroism (ICD) was not observed in the case of **7**. These results suggest that chirality of the QD moiety appears to be induced through chiral complexation. The crystal structure of (*R*,*R*)-**9**-*syn* revealed that the two [(L^2)Pd] units are bridged by the QD moiety of Q^1 as depicted in Figure 9. Each phenylene ring of Q^1 has an opposite dihedral angle of 47.3° with respect to the QD plane,

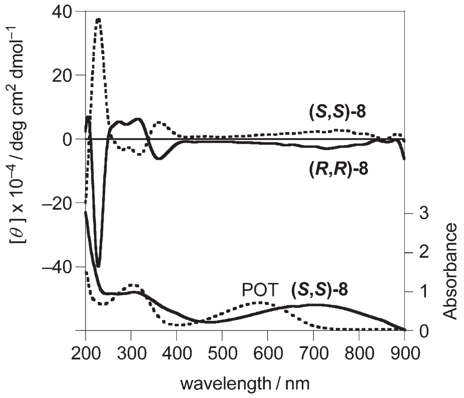
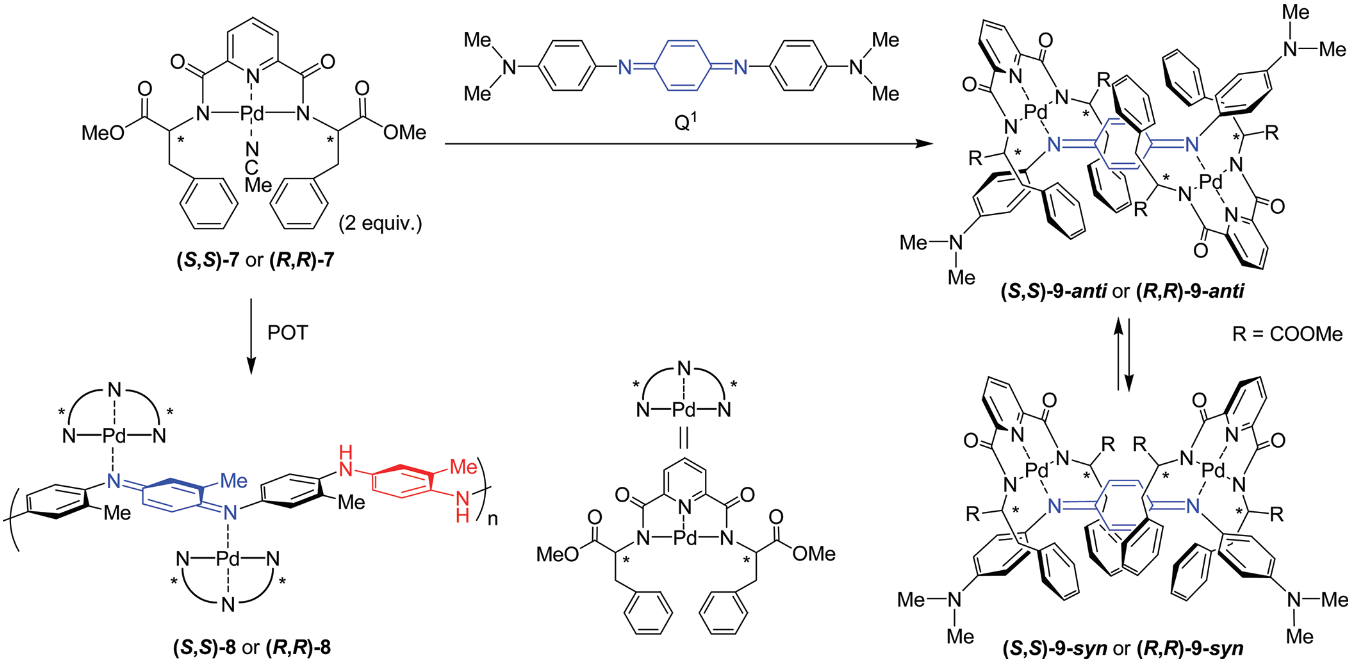


FIGURE 7. CD spectra (top) of **8** and UV−vis spectra (bottom) of (*S*,*S*)-**8** and POT in THF (1.3 × 10^{-3} M).

SCHEME 3. Formation of **8** or **9** with Q^1



causing a propeller twist of 75.6° between the planes of the two phenylene rings. The chirality of the podand moieties of [(L^2)Pd] is considered to induce a propeller twist of the π-conjugated molecular chain.

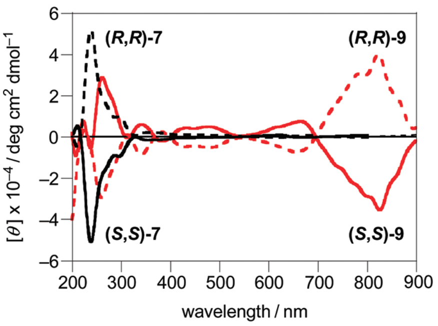
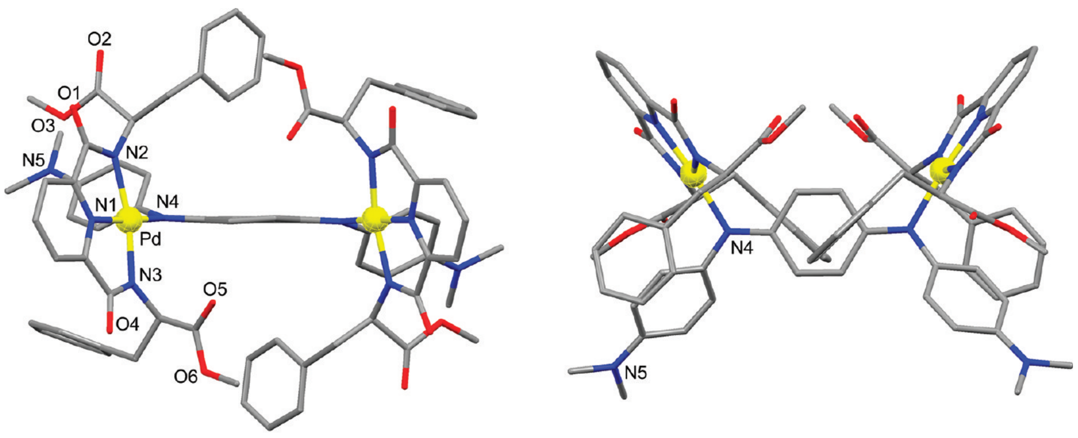


FIGURE 8. CD spectra of **7** (1.0×10^{-4} M) and **9** (0.5×10^{-4} M) in dichloromethane.

The redox conversion of PD to QD and the coordination ability of QD permitted the in situ oxidative complexation of PD with the palladium(II) complex **2** to form the 1:2 conjugated homobimetallic palladium(II) complex [(L^1)Pd(Q^2)Pd(L^1)] (**10**) (Scheme 4).[8b] The cyclic voltammogram of the conjugated complex **10** exhibited two separate redox waves at $E_{1/2} = -1.52$ and -0.78 V vs Fc/Fc$^+$ assignable to the successive one-electron reduction of the QD moiety. The crystal structure of **10**-*anti* revealed that the two [(L^1)Pd] units are bridged by the QD spacer (Figure 10).

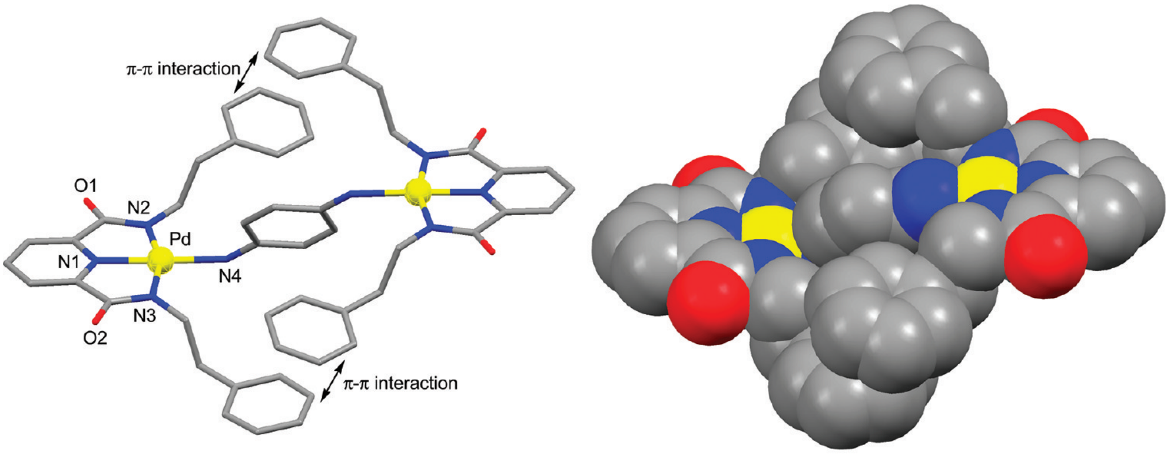
A conjugated complex containing a [M^{n+}(QD)M^{n+}] unit may, in principle, be converted to two other valence isomers, [$M^{(n+1)+}$(SQ)M^{n+}] or [$M^{(n+1)+}$(PDA)$M^{(n+1)+}$], which differ only in the electron distribution between the QD moiety and metals. This valence isomerization is considered to depend on the redox properties of both components.



(a)

(b)

FIGURE 9. (a) A top view and (b) a side view of the molecular structure of (*R,R*)-**9**-*syn* (hydrogen atoms are omitted for clarity).

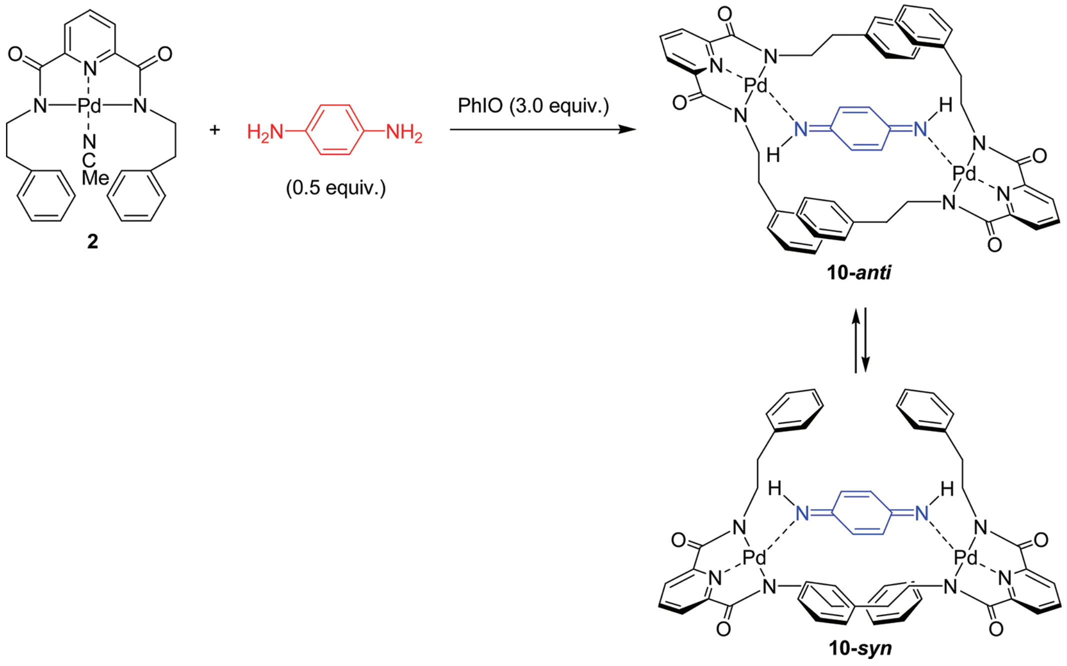


(a)

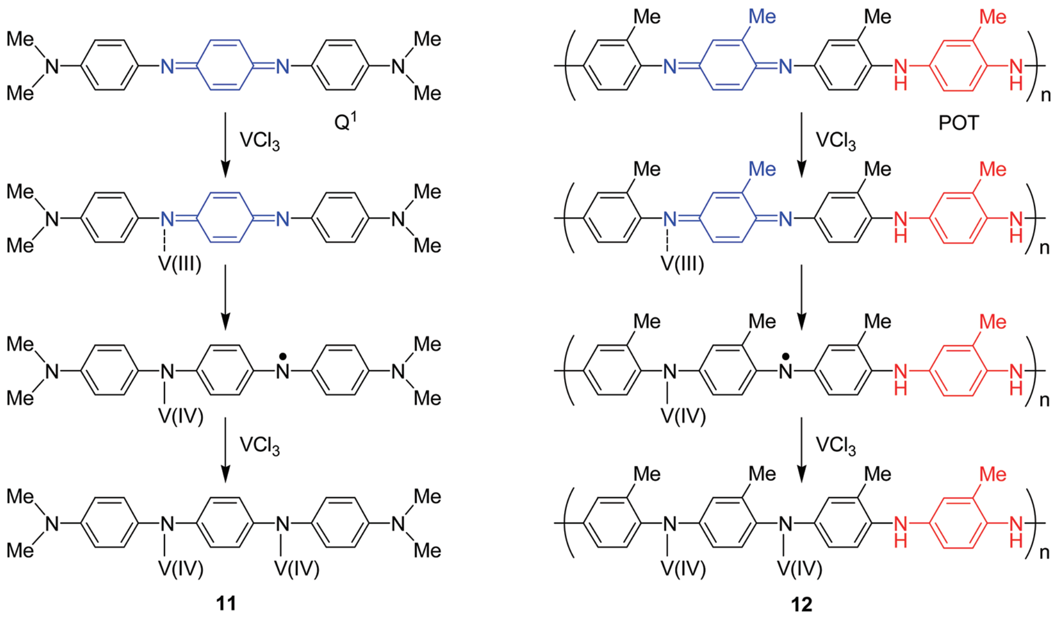
(b)

FIGURE 10. (a) The molecular structure of **10**-*anti* (hydrogen atoms are omitted for clarity). (b) Space-filling representation of the molecular structure of **10**-*anti* (hydrogen atoms are omitted for clarity).

SCHEME 4. Formation of **10** with Q^2

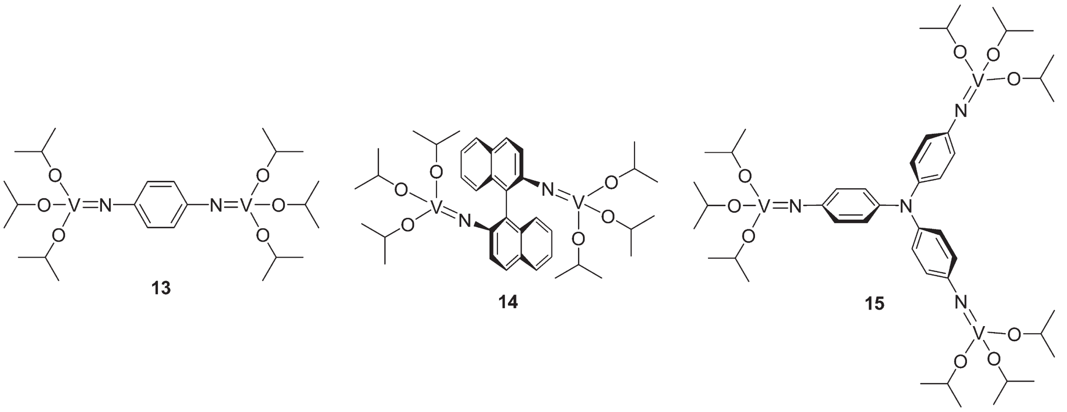


SCHEME 5. Complexation Behavior of (a) Q^1 and (b) POT with VCl_3



Vanadium compounds can exist in a variety of oxidation states and generally convert between the states via a one-electron redox process.[19] The π-conjugated molecule Q^1 and POT undergo complexation with VCl_3 together with redox reaction, affording the conjugated complexes **11** and **12**, respectively. The complexation proceeds via reduction of the QD moiety with oxidation of V(III) to V(IV), in which the vanadium species is considered to play an important role in both complexation and reduction processes (Scheme 5).[20]

The introduction of metal centers into π-conjugated molecules by imido bonds is considered to be a reliable strategy for the construction of conjugated systems. The imido ligand coordinates to metals through a metal–nitrogen multiple bond,[21] serving as an ancillary or supporting ligand. The imido ligands are known to be a particularly



13 **14** **15**

FIGURE 11. Multinuclear (arylimido)vanadium(V) alkoxides.

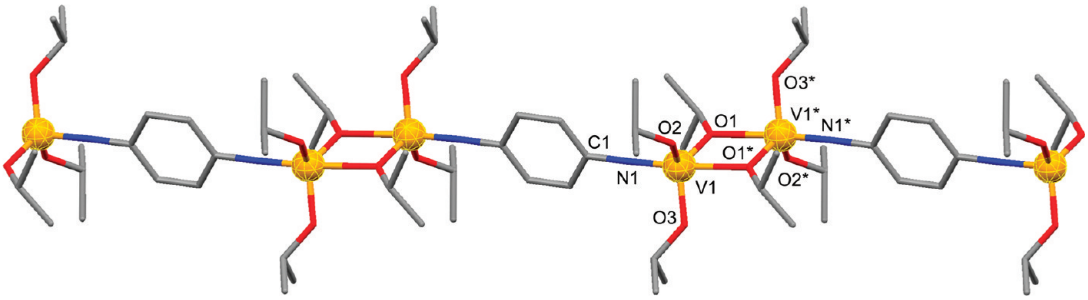


FIGURE 12. A portion of a layer containing the one-dimensional linear polymeric structure of **13** through μ-isopropoxido-bridging in the crystal packings.

suitable ligand for the stabilization of transition metal complexes in high oxidation states through extensive ligand-to-metal π donation.[22] Imidovanadium(V) compounds have attracted much attention because of their potential application as catalysts.[23] Self-association expands a multinuclear (arylimido)vanadium(V) compound containing the isopropoxide ligand through μ-isopropoxido-bridging in a crystal state. Conventionally, imidovanadium(V) compounds have been prepared by the reaction of oxovanadium(V) compounds with the corresponding isocyanates. One-pot preparation of (arylimido)vanadium(V) triisopropoxides from aniline derivatives by using NaH as a base was demonstrated to form self-assembling multinuclear (arylimido)vanadium(V) compounds.[24] This versatile one-pot preparation of (arylimido)vanadium(V) triisopropoxides is allowed to synthesize a variety of (arylimido)vanadium(V) triisopropoxides from aromatic amines. For example, the reaction of 1,4-phenylenediamine, $\text{VO(O}i\text{Pr)}_3$, and NaH afforded the binuclear (arylimido)vanadium(V) triisopropoxide, $[(i\text{PrO})_3\text{V(N-}p\text{-Ph-N)V(O}i\text{Pr)}_3]$ (**13**, Figure 11). The structure of **13** was confirmed by X-ray crystallographic analysis. Due to the conjugation, the V–N–Ph–N–V core is almost linear with the V(1)–N(1) distance of 1.678(2) Å and the V(1)–N(1)–C(1) angle of 177.8(1)°. As expected, the one-dimensional linear polymeric structure was formed through μ-isopropoxido-bridging in the crystal packing as shown in Figure 12.[25]

The axially chiral structure of the binuclear (arylimido)vanadium(V) triisopropoxide **14**, $[(i\text{PrO})_3\text{V(N-(}R\text{)-1,1}'\text{-BN-N)V(O}i\text{Pr)}_3]$, was confirmed by X-ray crystallographic analysis (Figure 13a,b).[24] As a result of the CH–π interactions, the binaphthyl moiety adopts a conformation with a dihedral angle of 78.99(9)° between the naphthalene planes. Two independent molecules exist in the asymmetric unit and are connected alternately through the intermolecular CH–π interactions, creating a left-handed helically ordered arrangement in the crystal packing as depicted in Figure 13c,d.

The crystal structure of the trinuclear (arylimido)vanadium(V) triisopropoxide **15**, $[\text{N}[(\text{-}p\text{-Ph-N)V(O}i\text{Pr)}_3]_3]$, revealed a tridendritic centrosymmetric structural motif with a distorted pyramidal geometry at the central nitrogen as depicted in Figure 14a.[24] The imido structure with the V(1)–N(1) distance of 1.657(3) Å and the nearly linear V(1)–N(1)–C(1) angle of 173.3(2)° indicates the higher participation of an sp-hybridized character in the nitrogen of the imido bond. Two mirror imaged molecules exist in the asymmetric unit, in which the

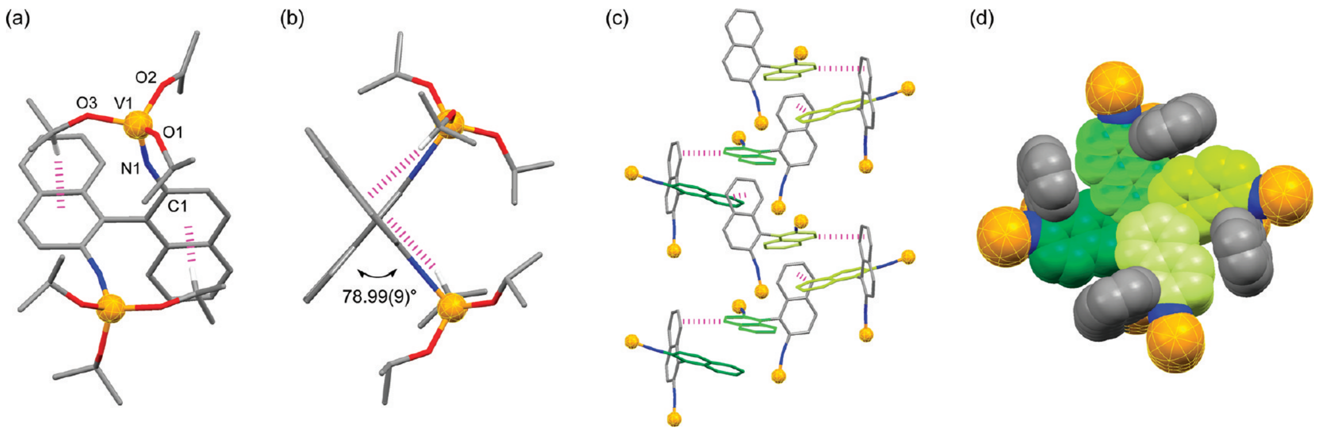


FIGURE 13. (a) Top view and (b) side view of the molecular structure of **14**, (c) side view of a portion of a layer containing the helically ordered molecular assembly through CH$-\pi$ interactions in the crystal packing of **14** (the isopropoxy groups are omitted for clarity), and (d) space-filling representation of a top view of the crystal packing of **14** (isopropoxy groups are omitted for clarity). The purple dotted line represents the intermolecular CH$-\pi$ interaction.

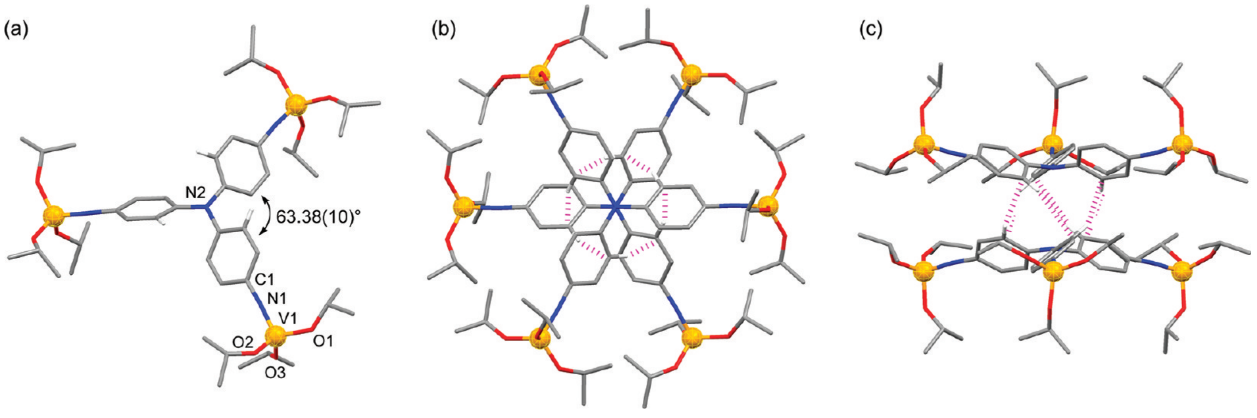


FIGURE 14. (a) The molecular structure of **15** and (b) top view and (c) side view of a "gear pair" like dimeric structure of **15** through six intermolecular CH$-\pi$ interactions. The purple dotted line represents the intermolecular CH$-\pi$ interaction.

triphenylamine moieties of these molecules adopt a mirror imaged propeller twist conformation. Instead of the μ-isopropoxido-bridged polymeric structure as observed in **13**, these molecules pack in a face-to-face manner to form a "gear pair"-like dimeric structure through six intermolecular CH$-\pi$ interactions between the aryl moieties in the crystal packing as shown in Figures 14b,c.

Modulation of Functional Properties of Conjugated Complexes with 1,4-Phenylenediamines or 1,4-Benzoquinonediimines

Bimetallic complexes composed of π-conjugated bridging spacers and terminal redox-active transition metals have received much attention as functional materials, in which electronic communication through a π-conjugated spacer is the focus.[1d,f,3] However, modulation of functional properties based on the redox states for such transition metals have been investigated in only few cases.[26] Terminal redox-active ferrocenyl groups were introduced into the redox-active PD bridging spacer (Scheme 6).[27] The crystal structure of $Q^3{}_{red}$ revealed a twist conformation of the PD moiety as shown in Figure 15. The PD derivative $Q^3{}_{red}$ was readily oxidized with PhIO to give the QD derivative $Q^3{}_{ox}$ as *syn*- and *anti*-QD isomers (1:1 ratio) (Scheme 6).

The $Q^3{}_{red}$ showed the successive one-electron oxidation processes of the ferrocene moieties, indicating the electronic communication between the ferrocenyl moieties through the PD bridging spacer. The corresponding equilibrium constant (K_c) for the comproportionation reaction ($[Fc-Fc] + [Fc^+-Fc^+] = 2[Fc^+-Fc]$) is 49. A simultaneous oxidation wave of two ferrocenyl moieties was observed in the case of the oxidized form $Q^3{}_{ox}$, wherein electronic communication between the terminal ferrocenyl moieties is suppressed. The regulation of the electronic communication was achieved by changing the redox states of the PD bridging spacer.

Complexation of Q^3_{ox} with the palladium(II) complex **2** led to the formation of the 1:2 conjugated homobimetallic palladium(II) complex $[(L^1)Pd(Q^3_{ox})Pd(L^1)]$ (**16**).[27] The crystal structure of **16** revealed that the two $[(L^1)Pd]$ units are bridged by the QD spacer to form the 1:2 complex **16-*anti*** in *anti* configuration as shown in Figure 16. In the case of **16**, no electronic communication was observed between the terminal ferrocenyl moieties.

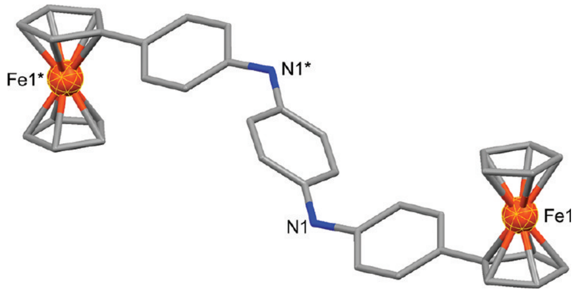
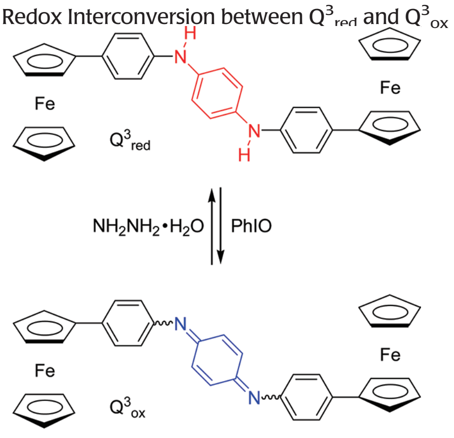


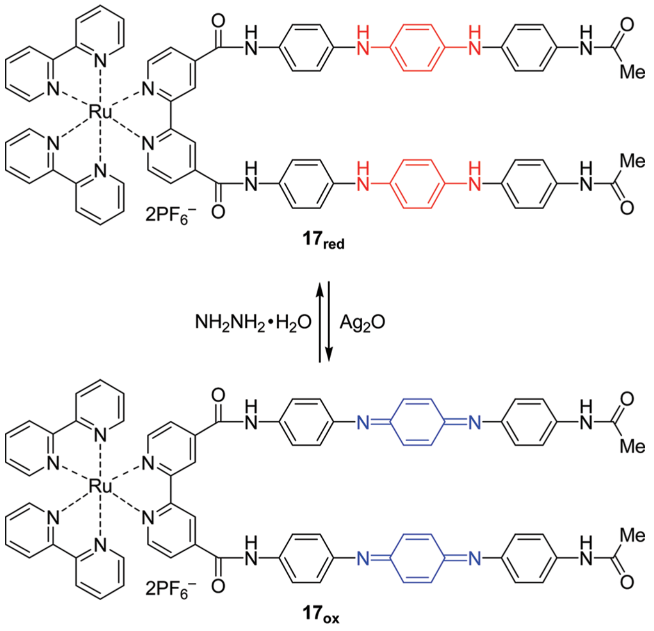
FIGURE 15. The molecular structure of Q^3_{red} (hydrogen atoms are omitted for clarity).

SCHEME 6. Redox Interconversion between Q^3_{red} and Q^3_{ox}



Bipyridyl ruthenium(II) complexes linked by a bridging spacer have been investigated electrochemically and photophysically to provide electronic and photoactive devices.[28] The redox interconversion between the ruthenium(II) complex $\mathbf{17_{red}}$ bearing PD moieties and $\mathbf{17_{ox}}$ bearing QD moieties is possible (Scheme 7).[29] In the emission spectrum of $\mathbf{17_{red}}$ excited at 477 nm, almost complete quenching was observed. An efficient photoinduced electron transfer is likely to operate in $\mathbf{17_{red}}$, where the reduced form of the π-conjugated pendant groups serves as an electron donor. Use of the oxidized form $\mathbf{17_{ox}}$ also resulted in a quenched spectrum upon excitation at 477 nm. Taking the reported electron-transfer

SCHEME 7. Redox Interconversion between $\mathbf{17_{red}}$ and $\mathbf{17_{ox}}$



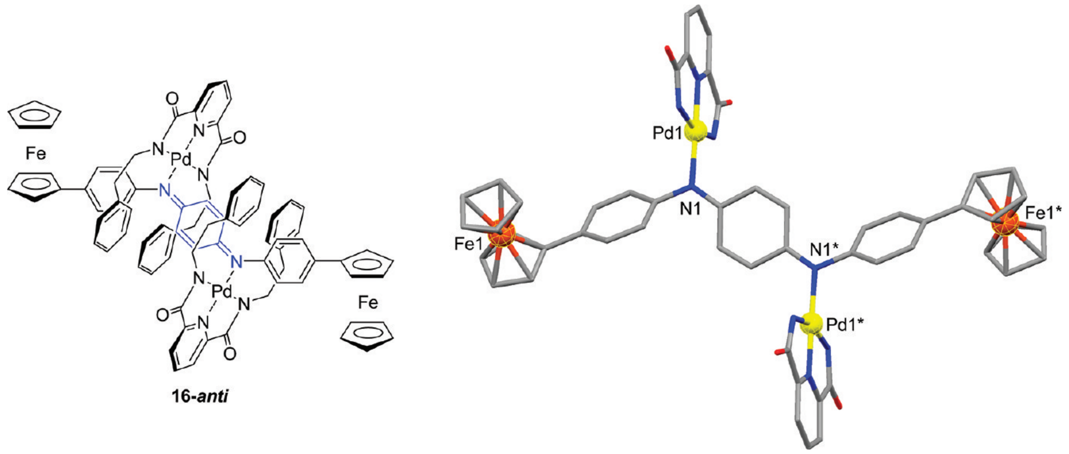
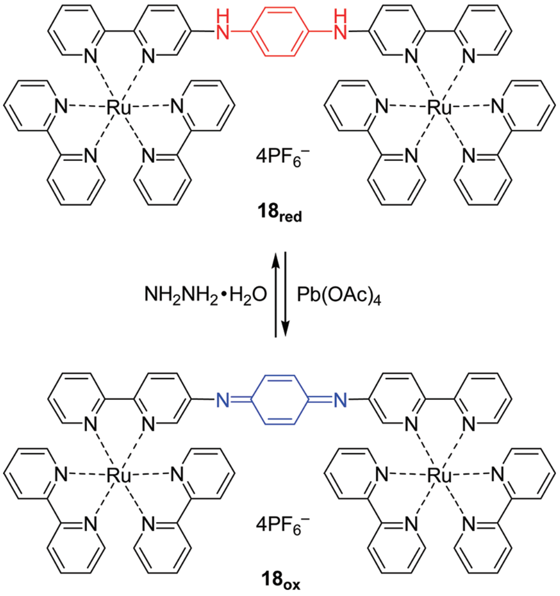
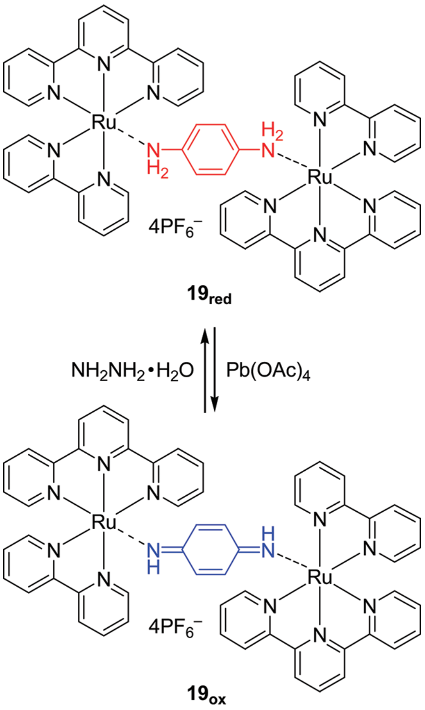


FIGURE 16. The molecular structure of **16-*anti*** (phenylethyl moieties and hydrogen atoms are omitted for clarity).

SCHEME 8. Redox Interconversion between $\mathbf{18_{red}}$ and $\mathbf{18_{ox}}$



SCHEME 9. Redox Interconversion between $\mathbf{19_{red}}$ and $\mathbf{19_{ox}}$



mechanism of complexes bearing viologen or benzoquinone moiety into account,[30] this result might be explained by electron transfer in a direction opposite to that of $\mathbf{17_{red}}$ or energy transfer. As observed in the ruthenium complex **17**, almost complete quenching occurred in both dinuclear ruthenium(II) complexes $\mathbf{18_{red}}$ and $\mathbf{18_{ox}}$ (Scheme 8).[31]

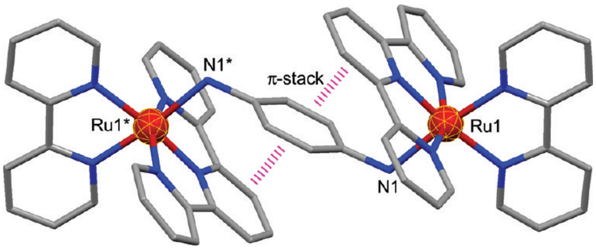


FIGURE 17. The molecular structure of $\mathbf{19_{red}}$ (hydrogen atoms are omitted for clarity).

Photoirradiation of (acetonitrile)(2,2′-bipyridine)(2,2′:6′,2″-terpyridine)ruthenium(II) hexafluorophosphate, [Ru(tpy)(bpy)-(CH_3CN)](PF_6)$_2$, in the presence of PD gave the conjugated ruthenium(II) complex [(tpy)(bpy)Ru(Q^4)Ru(tpy)(bpy)](PF_6)$_4$ ($\mathbf{19_{red}}$) in a one-pot reaction (Scheme 9).[32] The crystal structure of $\mathbf{19_{red}}$ revealed that the two [(tpy)(bpy)Ru] units are bridged by the PD spacer to form the C_2-symmetrical 1:2 complex $\mathbf{19_{red}}$ in *anti* configuration (Figure 17). The modulation of the emission properties of **19** by changing the redox states of the PD spacer was also performed. The reduced form $\mathbf{19_{red}}$ showed the emission at 605 nm in acetonitrile. On the contrary, almost complete quenching was observed in the emission spectrum of the oxidized form $\mathbf{19_{ox}}$.

Summary and Outlook

The π-conjugated polyanilines and QD derivatives are recognized as potential π-conjugated ligands or spacers based on the coordination ability of the QD nitrogen atoms. Another advantage depends on their redox properties. The QD moieties are reduced to semiquinonediimine radical anions (SQ) and phenylenediamine dianions (PDA). The combination of this redox behavior and complexation with transition metals provides efficient redox systems. The hybrid catalysts composed of π-conjugated polyanilines and metal nanoparticles can be designed based on this concept.[33] The controlled formation of the conjugated complexes with redox-active π-conjugated polyanilines and QD derivatives was achieved. Introduced metals play an important role as a metallic dopant and the complexed QD becomes stabilized as an electron sink. Furthermore, the chirality induction to a π-conjugated backbone of polyanilines and QD derivatives was performed by the complexation with optically active complexes, affording the chiral d,π-conjugated complexes. Another noteworthy feature of the conjugated complexes is the modulation of functional properties based on the redox states of the QD spacer. The conjugated complexes composed of the redox-active conjugated QD ligands are envisioned to provide not only functional electronic materials but also redox catalysts. By use of the one-pot preparation of (arylimido)vanadium(V) compounds from the corresponding anilines, the binuclear and trinuclear complexes were synthesized to permit the axial chirality and tridendritic centrosymmetric structural motif, showing their strong tendency to self-assemble through CH$-\pi$ interactions for the creation of a unique highly ordered molecular arrangement in a solid state. The above-mentioned redox systems are expected to provide promising nanomaterials and catalysts.

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BIOGRAPHICAL INFORMATION

Toshiyuki Moriuchi received his bachelor's degree in 1991 and his doctoral degree in 1995, both from Osaka University. He became Assistant Professor at Osaka University and was a postdoctoral fellow at California Institute of Technology with Professor Jacqueline K. Barton (1996−1997). Dr. Moriuchi was promoted to Associate Professor in 2004. His current research interests focus on the development of novel artificial bioconjugated systems and redox-active conjugated complex systems for functionalized catalysts and materials. He received the Inoue Research Award for Young Scientists in 1997.

Toshikazu Hirao was graduated from Kyoto University in 1973, where he obtained his doctorate in 1978. He became Assistant Professor at Osaka University and was a postdoctoral fellow at the University of Wisconsin with Professor Barry M. Trost (1981−1982). Dr. Hirao was promoted to Associate Professor in 1992 and Professor in 1994. He has been involved in the development of synthetic methodology and received the Chemical Society of Japan Award for Young Chemists in 1984. Dr. Hirao's current research interests lie in the area of the construction of an efficient system for electron transfer, which allows the development of new methods in organic synthesis, and novel redox-active systems consisting of transition metal complexes or π-conjugated polymers or oligomers including π bowls. These areas of research are correlated to the development of bioorganometallic conjugates. He received the Vanadius Award and the Award for Outstanding Achievements in Bioorganometallic Chemistry in 2008. He was director and is vice-president of the Chemical Society of Japan. He served as a head of the research project entitled "Construction of Dynamic Redox Systems Based on Nano-Space Control", Grant-in Aid for Scientific Research on Priority Areas, supported by the Ministry of Education, Science, Sports and Culture, Japan (2001−2003).

FOOTNOTES

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