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Controlled Formation of Synthetic Metal - Transition Metal Conjugated Complex Systems

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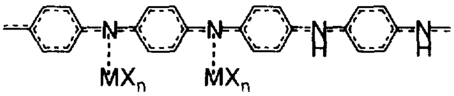
Abstract: The controlled complexation of the emeraldine base of poly(o-toluidine) with palladium(II) compounds was achieved in an organic solvent to afford structurally defined conjugated polymer complexes. Two coordination sites are used for complexation in the case of $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$, in contrast to only one coordination site available for the palladium(II) complex bearing the tridentate ligand. Two imine moieties are capable of participating in the complexation in the former case, possibly affording a cross-linked d,π-conjugated network system. On the contrary, a d,π-conjugated single-strand system is considered to be formed in the latter case.

Coordination of a transition metal to a π-conjugated organic molecule possessing relevant redox function is envisioned to provide a potentially important redox system depending on its complex structure and redox properties.[1] Multicoordination is expected to permit electronic communication between the metals through a π-conjugated chain. From these points of view, complexation with a π-conjugated polymer like polyanilines or polypyrroles has been demonstrated to afford such a system in a previous paper.[2] Copper salt is capable of contributing to the formation of the reversible redox cycle of undoped polyanilines.[3] An efficient catalytic system for the Wacker reaction has been achieved by utilization of polyanilines or polypyrroles as a redox-active ligand under oxygen.[4] A methodology has been sought to control the complexation behavior of π-conjugated polymers and elucidate their structures. We herein report the controlled complexation of poly(*o*-toluidine) in an organic solvent to afford structurally defined synthetic metal-transition metal conjugated complexes.



Treatment of the emeraldine base (the amine and imine moieties at ca. 1:1 ratio) of poly(*o*-toluidine)[5] in THF with a THF solution of $Pd(OAc)_2$ led to the red shift of the absorption around 590 nm, assignable to the CT band between the benzenoid and quinoid, in the UV-vis. spectra as shown in Figure 1.[6] The spectral change supports the formation of the polymer complex **1**, which was isolated by reprecipitation. The titration experiment showed the formation of the ca. 4:1 complex of the *o*-toluidine and palladium units. Similar complexation was also observed with $PdCl_2(MeCN)_2$ to afford the corresponding polymer complex.

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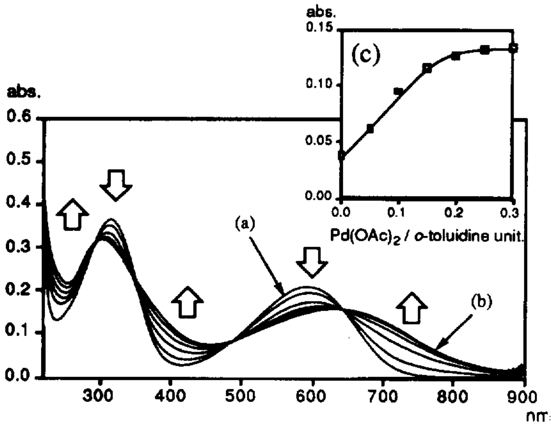


Figure 1. UV-vis. spectra in THF.
(a) Undoped poly(*o*-toluidine),
[*o*-toluidine unit] = 5.0×10^{-5} M.
(b) *o*-Toluidine unit : $Pd(OAc)_2$ = 4 : 1.
(c) Titration curve for plots of absorbance at 700 nm based on $Pd(OAc)_2$ / the *o*-toluidine unit.

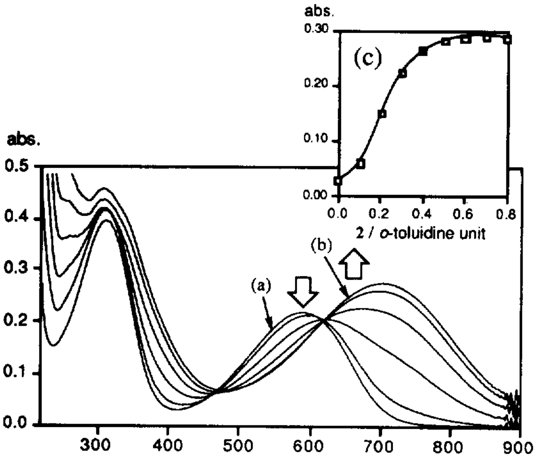


Figure 2. UV-vis. spectra in THF.
(a) Undoped poly(*o*-toluidine),
[*o*-toluidine unit] = 5.0×10^{-5} M.
(b) *o*-Toluidine unit : **2** = 2 : 1.
(c) Titration curve for plots of absorbance at 710 nm based on **2** / the *o*-toluidine unit.

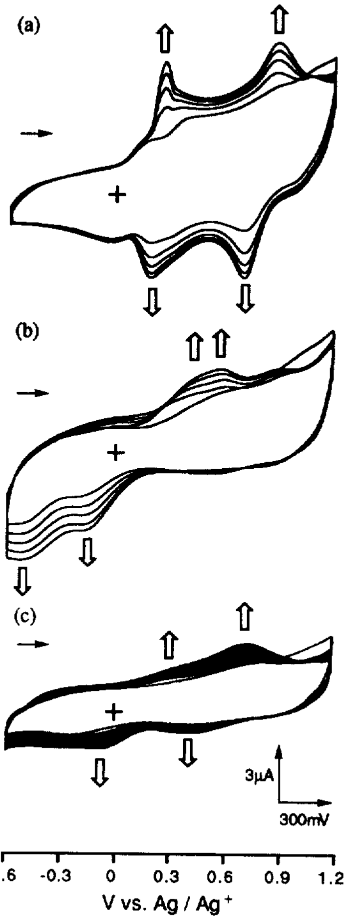
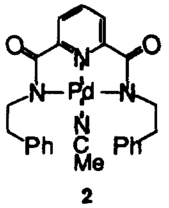


Figure 3. Cyclic voltammograms in THF under argon. [TBAP] = 0.1 M, scan rate: 100 mV/sec.
(a) Poly(*o*-toluidine),
[*o*-toluidine unit] = 1×10^{-3} M.
(b) Poly(*o*-toluidine)-$Pd(OAc)_2$,
[*o*-toluidine unit] = 1×10^{-3} M.
o-Toluidine unit : $Pd(OAc)_2$ = 4 : 1.
(c) Poly(*o*-toluidine)-BPHEPA-Pd,
[*o*-toluidine unit] = 1×10^{-3} M.
o-Toluidine unit : BPHEPA-Pd = 2 : 1.

Complexation with multidentate *N*-heterocyclic podand ligands has been developed in our laboratory to form the complexes with efficient redox function.[7] The palladium(II) complex **2** (BPHEPA-Pd), with a slightly distorted square planar geometry around the palladium, was obtained by complexation of the tridentate ligand, *N*,*N'*-bis(2-phenethyl)-2,5-pyridinedicaboxamide (BPHEPA) in acetonitrile. One coordination site possessing acetonitrile (solvent) is available for complexation with poly(*o*-toluidine). Treatment of poly(*o*-



2

toluidine) with the complex 2 actually resulted in a similar red shift of the CT band in the UV-vis. spectra (Figure 2) as observed above, despite the fact that the absorption maximum shifted further to around 710 nm. The thus-obtained complex 3 was indicated to consist of the *o*-toluidine and palladium units at ca 2:1 ratio.[6]

The complexation was also supported by cyclic voltammetry in solution.[8] The new oxidation waves appeared around 0.43 and 0.57 V, and 0.32 and 0.72 V vs. Ag/Ag$^+$ for the THF solutions of 1 and 3, respectively (Figure 3). The current value became bigger on repeating scans. A similar increase was observed only with poly(*o*-toluidine), possibly due to further polymerization of poly(*o*-toluidine) probably on electrode by electrolysis.

Palladium(II) species are suggested to coordinate to the imine moieties as illustrated in Figure 4 from the following observations. NMR spectra supported the formation of a complex of *N,N'*-diphenylquinonediimine with 2, but no typical complexation was observed with *N,N'*-diphenyl-1,4-phenylenediamine.[9]

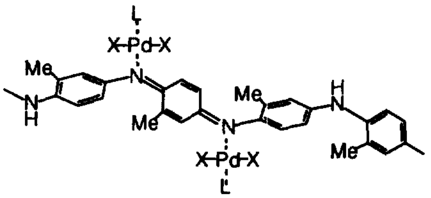


Figure 4. A proposed structure of poly(*o*-toluidine)-palladium(II) complex.

The difference in the ratio of the above-mentioned complexes 1 and 3 is explained by the coordination number of the palladium compounds available for complexation. Two coordination sites are used for complexation in the case of $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$, in contrast to only one coordination site available for 2. Two imine moieties of one or two polymer chains are capable of participating in the complexation with $Pd(OAc)_2$ or $PdCl_2(MeCN)_2$ to form the ca. 4:1 complex of the *o*-toluidine and palladium units since the emeraldine base of poly(*o*-toluidine) consists of the amine and imine moieties at ca. 1:1 ratio. A cross-linking is indicated in the former case to form a d,π-conjugated network system as illustrated in Figure 5. Such a cross-linking is not possible in the latter case to afford a d,π-conjugated single-strand system. Two different

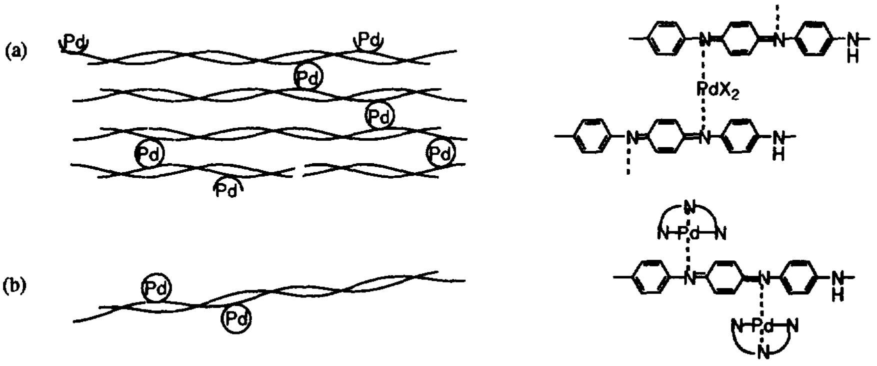


Figure 5. Complexation of poly(*o*-toluidine) with palladium(II) compound.
(a) Cross-linked structure. (b) Single-strand structure.

types of the conjugated complexes are complementary and formed only by changing the palladium(II) compounds.

In conclusion, we have demonstrated that the construction of the structurally defined synthetic metal-transition metal conjugated complexes is feasible in complexation of π-conjugated polymers, and their structures are reflected in the available coordination number of transition metals. Further investigation is now in progress.

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5. The polymer was prepared by chemical oxidation of *o*-toluidine with ammonium persulfate according to the reported procedure (MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. D. L. In *Conducting Polymers*, Alcacer, L., Ed.; Reidel Publ: 1987; p 105), followed by deprotonation with 1N NaOH aq. Although the thus-obtained polymer was mostly soluble in THF, the insoluble polymer was removed by filtration. Reprecipitation gave the polymer (number average molecular weight, ca. 3000 by GPC) used in this paper. Elemental analysis (elem. anal. $C_{7.00}H_{6.72}N_{0.98}$) indicates the emeraldine base structure consisting of the amine and imine moieties at ca. 1:1 ratio.
6. A solution (2.5 mL) of poly(*o*-toluidine) (1.05 mg) in THF (250 mL) was treated with a solution of $Pd(OAc)_2$ in THF at room temperature for 20 min under argon to give the spectra as shown in Figure 1. The complex (elem. anal. $C_{27.72}H_{29.35}N_{3.73}Pd_{1.00}$) was isolated by reprecipitation. The other complexes were prepared similarly. **1**: IR (KBr) 1588, 1490, 1411, 1311, 1154, 1104 cm^{-1}. **3**: IR (KBr) 1578, 1481, 1384, 1151 cm^{-1}.
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8. Cyclic voltammograms were obtained in a THF solution containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at room temperature under argon. Potentials were determined with a three-electrode system consisting of a glassy carbon electrode, a platinum auxiliary electrode, and an aqueous Ag/Ag^+ reference electrode at 100 mV/sec scan rate. The solution of the complex **1** was, for example, obtained by treatment of poly(*o*-toluidine) (0.52 mg) in THF (5 mL) with $Pd(OAc)_2$ in THF (2.5×10^{-4} mmol) at room temperature for 30 min under argon. Potentials are not corrected for the junction potential. For a 1.0 mM THF solution of ferrocene, the $E_{1/2}$ value was 0.62 V with the peak separation, 0.26 V.
9. X-ray crystallographic analysis of the complex of **2** with *N,N'*-bis(4'-dimethylaminophenyl)-1,4-benzoquinone diimine reveals that two palladium(II) species locate on both imine nitrogens.