Electrooxidative Polymerization of Tetraphenylporphinatoruthenium(II) Complexes with Diaza Compounds as Axial Ligands

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A "shish-kebab" type polymer film is formed by the two-electron oxidation of [Ru(tpp)L_2] (H_2tpp = tetraphenylporphine; L = *trans*-1,2-bis(4-pyridyl)ethylene, 4,4'-bipyridine, or 1,2-bis(4-pyridyl)acetylene) in 0.1 mol dm^{-3} (n-C_4H_9)$_4$N(ClO_4)–CH_2Cl_2. The polymers were characterized by cyclic voltammetry and UV-vis/IR spectrophotometry.

Recently, the polymeric macrocyclic metal complexes, including "shish-kebab" polymers, are attracting attention of material scientists as prospective organic conductors and superconductors. Over the last decade, a number of shish-kebab type metalloporphyrin polymers bridged by diaza compounds have been reported.[1-3] They have been synthesized chemically and obtained as powders. Here we report that several shish-kebab polymers can be readily formed as films on a substrate such as platinum through electrolytic oxidation of [Ru(tpp)L_2], where H_2tpp = tetraphenylporphine; L = *trans*-1,2-bis(4-pyridyl) ethylene (tbpe), 4,4'-bipyridine (bpy), or 1,2-bis(4-pyridyl) acetylene (bpa) (for ligand formulas, see Table 1). The present results are the first examples of electrochemical formation of shish-kebab polymers. Besides, tpp polymers of this type are hitherto unknown.

The ligands 4-phenylpyridine (ppy) and tbpe (Aldrich Chemical Co., Inc.) and bpy (Wako Pure Chemical Industries, Ltd.) were used without purification, while bpa was synthesized according to Tanner and Ludi.[4] The syntheses of [Ru(tpp)(tbpe)$_2$] (**1**), [Ru(tpp)(bpy)$_2$] (**2**), and [Ru(tpp)(bpa)$_2$] (**3**) were carried out as follows. An ethanolic solution of [Ru(tpp)(CO)(EtOH)][5] was irradiated with a high-pressure mercury lamp for about 90 min, while an argon stream was passed through it to help purge carbon monoxide. After the addition of an excess of axial ligand, the mixture was irradiated again for 10 min. The solvent was evaporated off, and the residue was dissolved in a small amount of chloroform and purified through column chromatography (silica gel–chloroform). The second fraction gave dark purple crystals on evaporation. The preparation of [Ru(tpp)(ppy)$_2$] (**4**) was carried out similarly, except that the solution was refluxed for 10 min after the addition of the ligand. The precipitate formed during this process was collected and was extracted into chloroform. The extract was evaporated to give reddish-brown crystals. The products were dried under vacuum. The yields were 40-50%.

The cyclic voltammogram of **1** (Figure 1, curve a) in 0.1 mol dm^{-3} (n-C_4H_9)$_4$N(ClO_4) (TBAP)—CH_2Cl_2 at a platinum disk electrode (1.6 mm diameter) showed two distinct oxidation waves at about 0.3 V and 1.3 V followed by a wave which merged with the final rise. The first was a one-electron reversible wave. Measurement of the UV-visible spectrum with an optically transparent thin-layer electrode cell[6] showed that the Q band (508 nm) decreased when **1** was oxidized at 0.5 V. This fact indicates that the first oxidation corresponds to the oxidation of Ru^{II} to Ru^{III}.[7] The second wave is thought to correspond to one-electron irreversible oxidation of the porphyrin ring, from the comparison of its potential with that of the second wave of **4**, of which the assignment of the second wave was established;[7] its excessively high peak height seems to be caused by overlapping of subsequent waves.

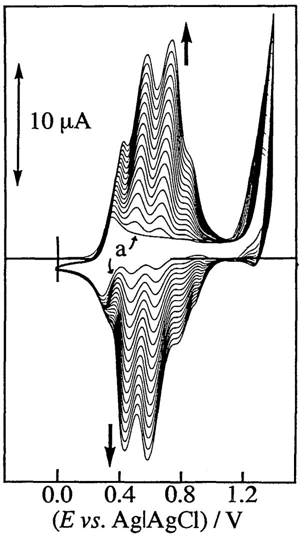


Figure 1. Multicyclic voltammogram of 1 mmol dm^{-3} solution of **1**. v = 200 mV s^{-1}.

The product of the second oxidation gave new reduction peaks at potentials between 0.35 V and 0.9 V; reoxidation peaks appeared on the second anodic sweep at the same potentials as those of the new reduction peaks. These new reduction peaks and the corresponding reoxidation peaks grew steadily on the subsequent sweeps (Figure 1). The characteristic sharp

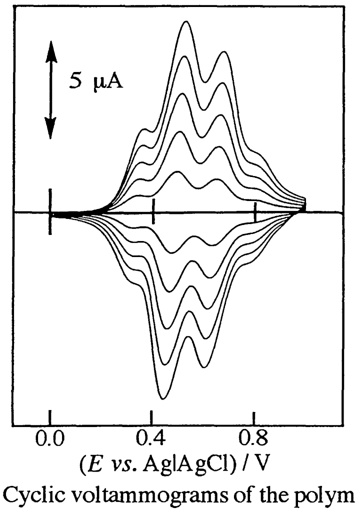


Figure 2. Cyclic voltammograms of the polymer of **1** in CH_2Cl_2 + 0.1 mol dm^{-1} TBAP without **1**. v = 100,80,60,40,20 mV s^{-1}.

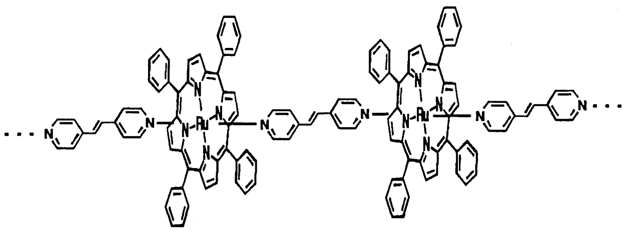


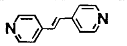
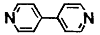
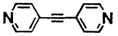
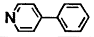
Figure 3. Structure of shish-kebab polymer of **1**.

triangular shape of these peaks indicates that an insoluble species deposited on the electrode was undergoing reversible redox processes. A brown film on the electrode could already be observed with naked eyes after several cycles of potential sweep. This film must be electroconductive, as indicated by the steady growth of the new peaks. The conductivity of the film was not yet measured, but it should not be very small, in view of the fact that the uncompensated resistance of the electrolytic circuit remained practically the same when the electrode was covered with an appreciable amount of the oxidation product.

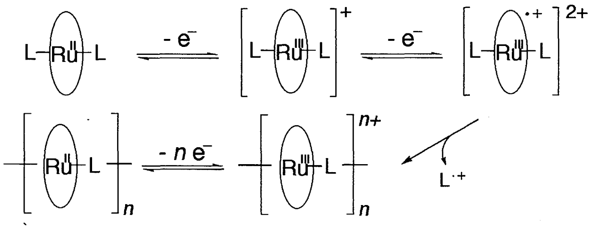
The deposited film was adherent, and the electrode with the film could be rinsed and transferred into another solution. The cyclic voltammograms in Figure 2 were recorded in this way with a film deposited by 6 cycles of potential sweep. The peak currents of each wave were proportional to the sweep rate, and the quantities of electricity transferred in the anodic and the cathodic processes were exactly the same, indicating that the film undergoes reversible redox processes. Very similar films were formed on the oxidation at a glassy-carbon and an indium doped tin oxide (ITO) glass electrodes as well. The film showed another reduction peak at about -0.7 V, followed by two or more obscure reduction peaks. The reduction at -0.9 V left the film virtually unchanged.

Among the three possible types of polymeric metalloporphyrins, i.e., metal-metal binding, ring-ring binding, and shish-kebab type, the film obtained here belongs to the last (Figure 3), as is inferred from the following observations. The UV-vis spectrum of the film deposited on an ITO glass electrode showed the Soret and Q bands characteristic of metalloporphyrins. The IR spectrum (KBr disk) of the film scratched off a platinum electrode showed a band at 1596 cm^{-1} that was much weaker than the corresponding band of **1**. This absorption is assigned to the centrosymmetric ring stretching mode of tbpe ligand that is IR active when the ligand is monodentate but inactive when it is didentate. The decrease of this band is widely regarded as evidence of shish-kebab type polymers bridged by tbpe and other diaza compounds.[1,2,8] Furthermore, the cyclic voltammogram of **4**, whose axial ligand lacks the second ligating position, showed no tendency of film formation on oxidation.

Table 1. The mid-potentials[a] of the complexes and polymers in 0.1 mol dm^{-3} TBAP–CH_2Cl_2 at 25 °C (unit, V)

L	[Ru(tpp)L_2]			Polymer		
	No.	Ox1	Ox2	Red1	Ox1	Ox2
	**1**	0.32	1.31[b]	– 0.70	0.51	0.68
	**2**	0.34	1.34[b]	– 0.76	0.60	0.74
	**3**	0.39	1.40[b]	– 0.64	0.58	0.72
	**4**	0.29	1.38	no deposition		

[a] {(1/2)(E_p^a+E_p^c) vs. Ag|AgCl(aq)}/V. The mid-potential of ferricinium/ferrocene couple was +0.50 V against this reference electrode. [b] Peak potential is cited.



Scheme 1.

The voltammetric behavior of **2** and **3** was quite similar to that of **1**. The mid potentials, (E_p^a + E_p^c)/2, of the monomers and the films (clear peaks only) are listed in Table 1. The UV-vis spectra of the films on an ITO glass electrode indicate that all the oxidation peaks of the films are attributable to metal oxidation. The splitting may be explained in terms of the stabilization of the mixed-valence state of Ru^{II}-Ru^{III}, as in the cases of chemically synthesized $[M(oep)(L)]_n$ (M = Ru, Os; H_2oep = octaethylporphine; L = pyrazine, bpy) described by Collman et al.[2]

A tentative polymerization mechanism is as follows (Scheme 1): from the product of the second oxidation, $[Ru^{III}(tpp^{\bullet +})(L)_2]^{2+}$, one of the axial ligand dissociates with a positive charge and the resulting $[Ru^{III}(tpp)(L)]^+$ polymerizes. The polymer thus formed should contain counter-anions and it can be reduced to a neutral polymer, probably releasing the counter-anions.

References and Notes

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9 Elemental Analysis of **1** Found: C, 75.22; H, 4.21; N, 10.10%. Calcd: C, 75.75; H, 4.49; N, 10.39%. **2** Found: C, 74.13; H, 4.40; N, 10.35%. Calcd: C, 74.92; H, 4.32; N, 10.92%. **3** Found: C, 75.16; H, 4.11; N, 9.75%. Calcd: C, 76.03; H, 4.13; N, 10.43%. **4** Found: C, 77.01; H, 4.40; N, 8.17%. Calcd: C, 77.40; H, 4.53; N, 8.21%.

FAB–MS: All parent peaks were observed.