Electroreduction of Dioxygen Using Co–Ru Dinuclear Porphyrin Catalyst in Nafion Film

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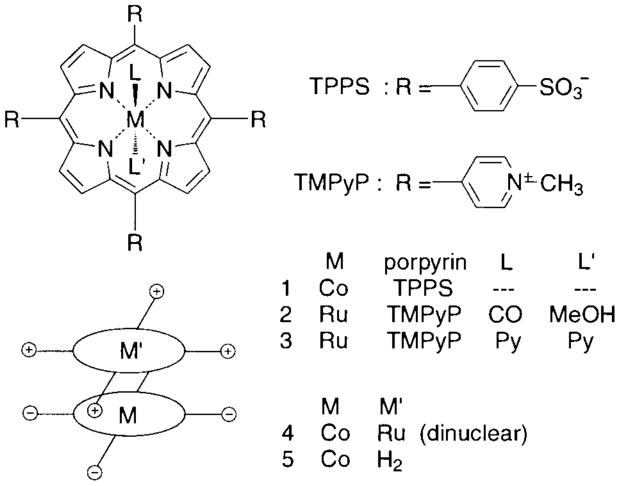
The mixing of CoTPPS with RuTMPyP (Figure 1) in water or organic solvents (DMSO, acetonitrile) results in dimerization through an electrostatic interaction. The dimeric porphyrin acts as an excellent catalyst for the 4-electron reduction of dioxygen in Nafion film, in which the multi-electron transfer is accelerated through the π-orbital overlapping.

The Co-porphyrin has been commonly investigated for the catalytic reduction of dioxygen[1] due to its higher redox potential, which leads to mimicing the reaction catalyzed by enzymes and to use the oxygen electrode in fuel cells. The reduction of dioxygen in water mainly provides two products, water and harmful hydrogen peroxide, through a 4-electron transfer and 2-electron one, respectively. A large activation barrier makes it kinetically difficult to allow the 4-electron reduction system. The 4-electron reduction of oxygen does not proceed using only the mononuclear Co-porphyrin. Polynuclear metal-complexes have been employed as an effective catalyst in the 4-electron reduction of dioxygen which provides H_2O either by a heterogeneous or homogeneous reaction, because multiple redox-active centers of metal ions accelerate the multi-electron transfer.[2,3] For the effective multi-electron transfer to dioxygen, molecular structures that undergo a sequential electron transfer should be designed on the basis of the redox potential, e.g., the polyaniline-Co-porphyrin complex[4] and tetra ruthenated Co-porphyrin.[5]

TPPS [*meso*-tetrakis(4-sulfonatophenyl)porphyrin] and TMPyP [*moso*-tetrakis(1-methyl-4-pyridinio)porphyrin] having ionic substituents are well-known to form a cofacial dimer with an ionic bond[6,7] and the distance between each porphyrin is estimated to be about 3–4 Å.[8] This close distance could provide the inner sphere electron transfer between each porphyrin that can electrically interact with each other through the π-electron on the porphyrin ring. On the other hand, RuTMPyP is expected to act as redox-active electron donor to CoTPPS which supplies electrons to the dioxygen, because Ru-porphyrin is well-known to be an excellent mediator. RuTMPyP is suitable for the formation of dinuclear Co–Ru porphyrins which retards self-aggregation due to the strongly coordinated axis ligand on ruthenium.

1 [Co^{II}(TPPS)][9,10] and **2** [Ru^{II}(TMPyP)(CO)(MeOH)][11] were prepared according to the literature method, and they were identified by their UV–vis, ^1H NMR and IR spectra. **3** [Ru^{II}(TMPyP)-$(Py)_2$] was synthesized from **2** through ligand exchange reaction by UV light irradiation[12] in pyridine, and confirmed by the disappearance of the IR absorption attributed to carbonyl group stretching vibration at 1930 cm^{-1}. After substituting carbonyl in pyridine, the redox wave of Ru^{II}/Ru^{III} appeared at 0.27 V vs Fc/Fc^+ in DMSO.

The dimerization of **1** with **3** were carried out with a mixed solution of each porphyrin in water or methanol. The precipitate was filtered and dried (dinuclear complex **4**). The dimerization reaction was confirmed by Job's titration[6,7,13] using UV–vis spectrum. During the titration, the Soret band of the porphyrins was reduced and shoulder peak appeared in the longer wavelength region of the Soret band. The minimum peak of the job plots at $x = 0.5$ indicates the predominant formation of the dinuclear complex. The dimerization constant, K_d, of Ru(II)–Co(III) was estimated to be 2×10^6 mol^{-1} dm^3 in aqueous solution by a curve fitting method with the theoretical equilibrium line. The dinuclear complex **4** was also identified with the MALDI-TOF-mass spectrum at $m/z = 1766$.



	M	porpyrin	L	L'
1	Co	TPPS	---	---
2	Ru	TMPyP	CO	MeOH
3	Ru	TMPyP	Py	Py

	M	M'
4	Co	Ru (dinuclear)
5	Co	H_2

Figure 1. Structures of water soluble metalloporphyrins.

To investigate the electrochemistry of these porphyrins in the homogeneous polymer film, the cyclic voltammetry of **1** and **4** (9.5×10^{-5} mol cm^{-3}) in the Nafion film, which was prepared by the spin cast method on GC electrode, was carried out in 0.5 mol dm^{-3} $HClO_4$ + 0.1 mol dm^{-3} NH_4PF_6 aqueous solution under a saturated N_2 atmosphere. The modified electrode was prepared as follows. Two milliliters of 5 wt% Nafion perfluorinated ion-exchange resin solution (purchase from Aldrich) in which porphyrin is dissolved at 4.8 mol dm^{-3}, deposited on the GC electrode and dried at room temperature with rotation of electrode at 500 rpm. The disk electrode has an area of 0.28 cm^2. Dinuclear porphyrin **4** is physically mixed in Nafion matrix in which these porphyrins also form dinuclear complexes as observed by UV–vis spectrum. It is confirmed by UV–vis spectra changes same as in aqueous solution. The Nafion film of **4** shows only a single wave at 0.19 V vs SCE though the redox potentials of **1** and **3** in DMSO are –0.33 V and 0.27 V vs Fc/Fc^+, respectively[14]. The cyclic voltammogram of **1** reveals a redox wave corresponding to the Co(II/III) redox couple at 0.20 V vs SCE, which does not agree with that of **4**. The peak current and passing charge of the cyclic voltammogram of **4** are two times greater than that of **1**. Double concentration of **1** shows about the same redox current as **4**, however, the peak separation between oxidation and reduction is larger than that of **4**. It means existence of charge transfer from ruthenium to cobalt in dinuclear complex **4** and acceleration of electron transfer rate at the surface of electrode. The non-linear relation of i vs $v^{1/2}$ reveals that the redox reaction is not completely rate-determined by diffusion. As the control experiment, the Co-H_2 porphyrin dimer **5** shows less redox activity than **1**. These results indicate that the redox wave of **4** involves 2-electron transfer process corresponding to the Ru–Co(II-II/III-III) redox couple.

To quantitatively evaluate the rate of electron transfer of **4**, the apparent diffusion coefficients, D_{app}, was determined by potential-step chronoamperometry. The Cottrell equation is employed in the limiting diffusion system.[15] The value of D_{app} was determined to be 3×10^{-10} cm^2 s^{-1}(**4**) by curve fitting simulation, which is about ten times greater than that of **1** (2×10^{-11} cm^2 s^{-1}). The thickness of the Nafion film was 1.8×10^{-5} cm from the previously reported density of Nafion[16]. The results supported the idea that the electron transfer of CoTPPS is accelerated by the complexation with RuTMPyP, that is, ruthenium act as an excellent electron mediator.

The catalytic behaviors of **4** for the reduction of O_2 in acidic solution was studied using rotating disk voltammetry (RDV)[17,18] and rotating ring disk voltammetry (RRDV) on a Nafion modified GC electrode in an air saturated atmosphere. The homogeneous polymer catalyst film (**4** : 9.5×10^5 mol cm^{-3}) with interference stripes was prepared by the spin cast method. In air, a catalytic current was observed at $E^{1/2}$ = 0.16 V vs SCE in RDV (150 rpm). The quantitative kinetic data on the basis of the Koutecky–Levich equation resulted in a 4-electron transfer of n = 3.9 for the dioxygen reduction as shown in Figure 2, whereas ruthenium porphyrin itself shows no catalytic current. The water formation through the 4-electron reduction of O_2 is supported by RRDV in which H_2O_2 could be detected as a side product through a 2-electron transfer. Number of electrons transferred can be calculated from the slope of the Koutecky–Levich plots (RDV)[17,18] and selectivity of 4-electron reduction is $[(N_0 - N)/(N_0 + N)]$ where N_0 and N are collection efficiency of $\mathrm{Fe(CN)_6}^{4-/3-}$ and O_2 reduction, respectively (N_0 = 0.39, potential of ring electrode = 1.0 V vs SCE). A large amount of H_2O_2 formation was not observed in the catalytic system and the selectivity for the 4-electron transfer was determined to be >95%. The collection efficiency of H_2O_2 did not depend on the rotating rate, which means oxygen reduction through sequential 4-electron transfer. On the contrary, the mono-nuclear complex **1** shows much lower selectivity for the 4-electron reduction. The number of electrons transferred was determined to be n = 2.4 and **5** also provides a low selectivity for the 4-electron reduction (n=2.6). The 2-electron reduction of O_2 is dominated in the catalytic system of the mono-nuclear **1** or **5**. These results supported the idea that the Ru porphyrin promotes the fast electron transfer by acting as an electron mediator to the Co porphyrin.

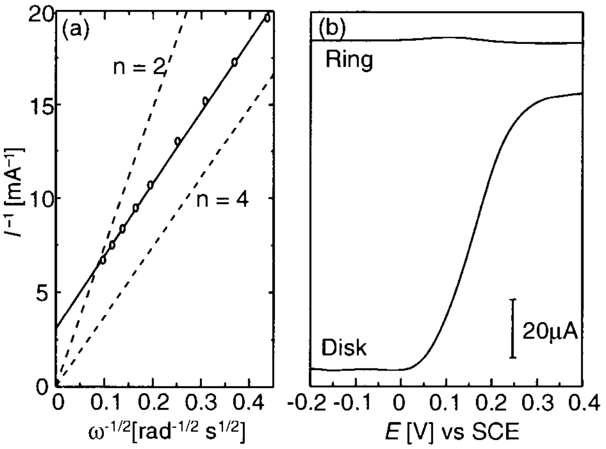


Figure 2. (a) Koutecky—Levich Plots (RDV) catalyzed by **4**, solid line is experimental plots, dashed lines are caluculated ones, $v = 20$mV s^{-1}, $D_{O2} = 1.7 \times 10^{-5}$cm^2 s^{-1}, $C_{O2} = 0.28$m mol L^{-1}, $A = 0.28$cm^2, (b) RRDV of O_2 reduction catalyzed by **4** (150rpm), $v = 20$mV s^{-1}.

In conclusion, the dinuclear complex **4** in the Nafion film sufficiently acts as heterogeneous catalyst for the 4-electron reduction of O_2, which is caused by the fast electron transfer from the electrode to the dioxygen. The ruthenium porphyrin **3** itself shows no catalysis for the dioxygen reduction, therefore, **3** should act to quickly supply multiple electrons to **1** through the π–π interaction of **3** with **1** by ionic groups that enhance the fast and stable multi-electron transfer for the reduction of dioxygen.

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13 $F(x)$ is directly proportional to the reaction efficiency which could be estimated by fitting theoretical equilibrium lines into the observed Job plots.
14 Redox potential of Ru(II/III) is 0.43 V vs SCE (RuTMPyP is adsorbed on GCE). Redox potential of CoTPPS in Nafion film is 0.19 V vs SCE.
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