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Reversible Oxygen-Releasing from the Composite of Picketfence-Porphyrinatocobalt and Carbon in Response to a 1.5 V-Application

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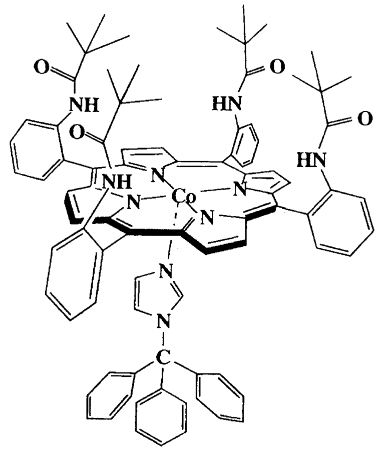
5,10,15,20-Tetrakis(α-*o*-pivalamidophenyl)porphyrinatocobalt(II) (CoP) complexed with *N*-tritylimidazole in the solid state quickly and reversibly absorbed oxygen from air (14 cm^3 O_2/g), which was ascribed to a Co/dioxygen 1/1 adduct formation. The adduct formation was an exothermic reaction, and the absorbed oxygen was released above 65 °C. A disk (e.g., diameter 2 cm×2 mm) was prepared with powders of the oxygen-absorbing, but electrically insulating, CoP complex and of electrically conductive carbon. The application of 1.5 V to the disk induced a temperature elevation in the disk, which momentarily released the absorbed oxygen. The oxygen-releasing and -absorbing cycle could be repeated more than 100 times, with a 5-min switching on-off interval under ambient conditions.

Porphyrinatocobalts(II) with a cavity structure on the porphyrin plane specifically bind oxygen to reversibly form a Co/dioxygen 1/1 adduct.[1] A typical example is the 5,10,15,20-tetrakis(α-*o*-pivalamidophenyl)porphyrinatocobalt(II) or picketfence porphyrinatocobalt(II) of Collmam (Scheme 1, CoP).[1a,2] This porphyrin has four pivalamido groups on one side of the plane to provide a cavity for oxygen-binding, leaving the other side for ligating an imidazole to the central cobalt(II) ion of porphyrin. The cavity structure inhibits an irreversible side-reaction via μ-dioxodimer formation, and the ligated imidazole improves the affinity with the bound dioxygen. The oxygen-binding by the CoP-imidazole complex is also characterized by its kinetic activity in the reaction, even in the solid state, which is caused by the five-coordinated structure of porphyrinatocobalt(II) or the vacant sixth site for oxygen-binding.



Scheme 1.

We have been studying porphyrinatometals as an efficient oxygen carrier and applying them to an oxygen absorbent,[3] an oxygen-permselective membrane,[4,5] an oxygen sensor,[6] and artificial hemoglobin.[7] Among them, the authors have demonstrated selective oxygen absorption in solid porphyrinatocobalt(II) and oxygen-enrichment from air using a pressure-swing absorption experiment.[3] On the other hand, we recently reported an oxygen-releasing disk made of an oxygen-absorbing, but electrically insulating, cobalt chelate, (*N*, *N*′-disalicylideneethylenediamine)cobalt(II) [Co(salen)], and an electrically conductive carbon powder.[8] The composite disk selectively absorbed oxygen from air and released the absorbed oxygen in response to the application of 6 V to the disk. The oxygen absorption by [Co(salen)] is an exothermic reaction with an enthalpy of ca. 30 kcal mol^{-1}.[9] The voltage application induced a temperature elevation to ca. 80 °C, which reduced the oxygen adduct formation and quickly released the absorbed oxygen. The oxygen-releasing and -absorbing processes could be repeated under ambient conditions. However, there remained two issues to be improved: (i) The temperature of the disk was required to be elevated to ca. 80 °C with a 6 V-application because [Co(salen)] formed a stable μ-dioxo complex or Co/dioxygen 2/1 adduct via a strong exothermic reaction. A smaller temperature elevation or the application of a lower voltage is expected as a more favorable stimulus to release the absorbed oxygen from the disk. (ii) In contrast to the quick oxygen release, the re-absorption of oxygen took several hours and 30 min for the [Co(salen)] disk and the disk containing the 3-ethoxy derivative of [Co(salen)], respectively. A rapid oxygen re-absorption or re-generation of the disk is desirable as a feasible oxygen-releasing device.

In this work, we prepared a disk of a composite of the CoP complex and carbon powder, and demonstrated oxygen-release in response to a 1.5 V-application and rapid re-absorption of oxygen; e.g., an oxygen release and -absorbing

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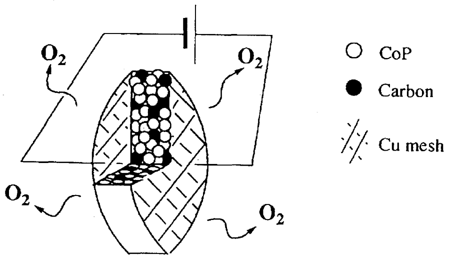

Scheme 2.

cycle with a 1.5 V-switching on-off for a 5 min interval (Scheme 2).

Experimental

Materials. 5,10,15,20-Tetrakis(α-*o*-pivalamidophenyl)porphyrinatocobalt(II) CoP) was synthesized as described in the literature.[2] *N*-Tritylimidazole (TIm) was prepared according to the literature[10] by refluxing sodium imidazolate (7 g) and triphenylmethyl bromide (25 g) in toluene (100 cm^3) for 48 h. The crude product was purified by column chromatography on silica gel with a chloroform/ethyl acetate (1/4) solvent (R_f = 0.43). Recrystallization from xylene yielded TIm (3.3 g) as needle-like crystals (mp 220 °C). *N*-Benzylimidazole and *N*-methylimidazole were purified by recrystallization (mp 69 °C) and distillation (bp 198 °C), respectively.

The CoP complex with TIm was prepared by mixing CoP (0.15 g, 0.14 mmol) and TIm (0.65 g, 2.1 mmol) in THF (15 cm^3) under a nitrogen atmosphere. After the addition of a small amount of hexane, the solution was allowed to stand for one day. The crystals were washed with hexane, then heated at 80 °C in vacuo for 1 d to completely remove the solvent (yield 0.11 g). The purity of the CoP-TIm crystals was checked by its visible absorption (λ_{max} = 527 nm, $\varepsilon = 4.6\times10^3\ \mathrm{M^{-1}\,cm^{-1}}$).

The carbon powder was purchased from Fujikura Chemical Co.; specific gravity 0.9—1.0. It was washed several times with hexane, dried in vacuo, and sieved into the narrow particle size range of 32—45 μm.

Disk Preparation. The crystals of the CoP–TIm complex were ground, then sieved into the particle size range of 32—45 μm. The CoP–TIm powder and the electrically conductive carbon powder were mixed, sandwiched between copper meshes, and pressed under 120 kg cm^{-2} pressure for 3 min, to produce the CoP/carbon disk, e.g., 2 cm diameter, 2 mm thickness for 0.24—0.40 g CoP–TIm and 0.16—0 g carbon. The electrical resistance of and temperature on the disk under the applied voltage were measured with a multitester and a thermister thermometer, respectively.

Gas Absorption Measurements. The absorbed amounts of oxygen and nitrogen to the powder of the CoP complex were measured based on the pressure decrease with a Baratron absolute pressure gauge (MKS Instr. KA-102) under the condition of constant volume. The apparatus consisted of a vacuum line mounted in a thermocontrolled air bath.

Oxygen-releasing and -absorbing from and onto the disk in response to an applied voltage were measured as follows. The disk was put into a 50 cm^3 vessel at a constant pressure of 1 atm. The oxygen concentration in the vessel was measured with an oxygen sensor (Koumei Co., Japan, OM-511).

Spectroscopic Measurements. Imidazole-ligating to CoP and oxygen-binding to the CoP complex were measured by spectral changes in their visible absorption using a UV spectrophotometer (JASCO V-550). Oxygen-adduct formation of the CoP powder and of the CoP composite in the disks were measured using the UV spectrophotometer equipped with a reflectance apparatus.

Results and Discussion

N-Tritylimidazole (TIm) was selected as the imidazole ligand (L) of CoP to form the five-coordinated CoP–L with oxygen-binding capability based on the following two experimental results. First, the ligating equilibrium constant of an imidazole to CoP (Eq. 1) was estimated by spectroscopic titration of CoP with an imidazole in toluene. The visible absorption spectrum of CoP with λ_{max} = 524 nm was changed by the addition of imidazole to the spectrum with λ_{max} = 527 nm assigned to a five-coordinated porphyrinatocobalt(II). The spectrum of the CoP–L complex had no shoulder absorption ascribed to the six-coordinated porphyrinatocobalt(II) even after the excess addition of imidazole; CoP preferentially forms the five-coordinated CoP–L complex to give the equilibrium constant K^L of Eq. 1 (Table 1). K^L for TIm was larger than those for *N*-benzylimidazole and *N*-methylimidazole, and a small excess of TIm was enough to form the five-coordinated CoP–TIm complex. This leads to be the following two advantages for the CoP–TIm powder as an oxygen absorbent: large absorption amount of oxygen per gram of absorbent and low evaporative loss of the imidazole added in excess during the experiment.

$$\mathrm{CoP} + \mathrm{L} \xrightleftharpoons{K^{\mathrm{L}}} \mathrm{CoP{-}L} \qquad (1)$$

Secondly, the oxygen-binding affinity (p_{50}: the oxygen partial pressure at 50% of oxygen-binding) or the equilibrium constant in the oxygen-binding reaction (Eq. 2) of the CoP complexes was also determined in toluene from the oxygen-binding equilibrium curves which were drawn based on the visible spectral change of the CoP complexes in response to the oxygen partial pressure (λ_{max} = 527 and 548 nm for deoxy and oxy, respectively). The curves obeyed Langmuir's isotherms, which gave the p_{50} values listed in Table 1. The oxygen-binding affinity of the CoP–TIm complex was larger (p_{50} was smaller) than that of the CoP complex with methylimidazole. The large oxygen-affining of the CoP–TIm complex brings about a great difference in the degree of oxygen-binding (or the oxygen releasing amount in this experiment) between the oxygen-absorbing and -releasing processes.

$$\mathrm{CoP{-}L} + \mathrm{O_2} \xrightleftharpoons{1/p_{50}} \mathrm{O_2{-}CoP{-}L} \qquad (2)$$

Table 1. Imidazole-Ligating Constant (K^L) and Oxygen-Binding Affinity (p_{50}) of the CoP Complex in Toluene and Oxygen Absorption Amount onto the CoP Complex in Solid State under Oxygen (25 °C)

Imidazole	$10^{-4}K^L$	p_{50}	O_2 Abs
	M^{-1}	cmHg	$cm^3\ g^{-1}$
Methylimidazole	1.7	14	10
Benzylimidazole	1.8	4.2	16
Tritylimidazole	3.7	7.8	14

In addition, TIm is non-volatile, which is absolutely necessary during the temperature elevation and gas absorption–desorption experiment.

The isolated CoP–TIm complex was ground and sieved. The oxygen absorption onto the CoP–TIm powder was rapid and reached equilibrium within one minute. The absorption isotherm of oxygen for CoP–TIm in the solid state is shown in Fig. 1. The isotherm obeyed a Langmuir one. The oxygen-binding affinity, determined by the Langmuir isotherm, was $p_{50} = 3.9$ cmHg (at 30 °C, 1 cmHg = 1333.322 Pa); this affinity was greater than that in the toluene solution (Table 1) and could be reduced by taking into account the oxygen solubility in toluene. The oxygen absorption amount under oxygen ($p_{O2} = 76$ cmHg) was 14 $\mathrm{cm^3\,g^{-1}}$ CoP–TIm, which corresponded to 84 mol% of the fed CoP–TIm in the measurement. This oxygen absorption amount was ca. 20-times greater than the physical adsorption amount of nitrogen at $p_{N2} = 76$ cmHg. Figure 1 also shows the oxygen absorption by the CoP/carbon composite disk. The CoP–TIm complex in the composite also selectively absorbed oxygen, and the absorption amount was in fair agreement with the CoP content in the disk. The CoP–TIm powder and the CoP/carbon composite acted as efficient oxygen absorbents.

The powders of the CoP–TIm complex and of the electrically conductive carbon were mixed, and the disk (2 cm diameter×2 mm thickness) sandwiched between copper meshes was prepared. Homogeneous mixing of CoP–TIm and carbon was recognized by the homogeneous deep reddish color of the broken pieces of the disk and by the homogeneous Co distribution in the disk by X-ray microanalysis. The disk was not mechanically tough, but remained intact during the following repeated temperature elevation and depression (70 °C to room temperature) or oxygen-releasing and -absorbing tests.

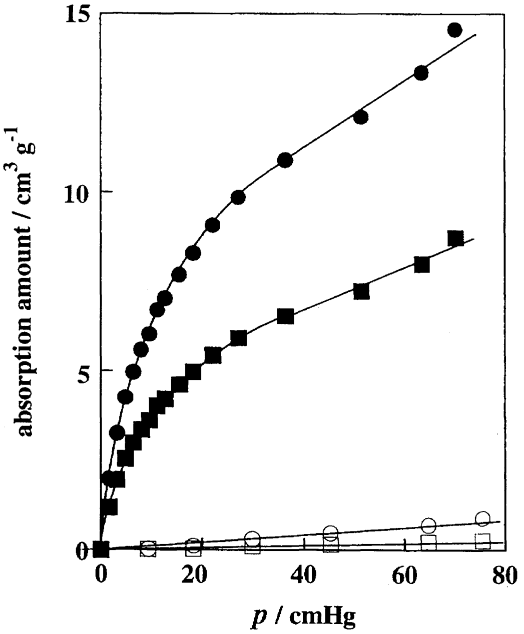

Fig. 1. Absorption isotherms of oxygen (closed plots) and nitrogen (open plots) for the CoP–TIm complex in the solid state (circle plots) and for the CoP/carbon disk (CoP–TIm content = 63%) (square plots) at 30 °C. *p*: partial pressure of oxygen for the closed plots and nitrogen for the open plots, respectively.

The 63% CoP–TIm/carbon composite disk absorbed 9.0 $\mathrm{cm^3}$ oxygen per gram of composite at room temperature (Fig. 2). The oxygen-binding affinity was reduced with an increase in temperature for CoP–TIm and the composite. Enthalpy and entropy changes (ΔH and ΔS) for the oxygen-binding of the CoP–TIm powder in the solid state were determined from the temperature dependence of p_{50}, to give $\Delta H = -13\ \mathrm{kcal\,mol^{-1}}$ and $\Delta S = -38\ \mathrm{cal\,deg^{-1}\,mol^{-1}}$. The oxygen-binding for CoP is an exothermic reaction, but not as strong as that for [Co(salen)], which reduces the temperature elevation in the composite disk required to cause a complete release of the absorbed oxygen (65 and 80 °C for the CoP and [Co(salen)] composite disk, respectively).

A 1.5 V potential (one dry cell) was applied to the disks with various compositions of CoP–TIm and carbon. Table 2 shows the electrical resistance and heat elevation of the disks. Although the disks containing >70% CoP–TIm had an ex-

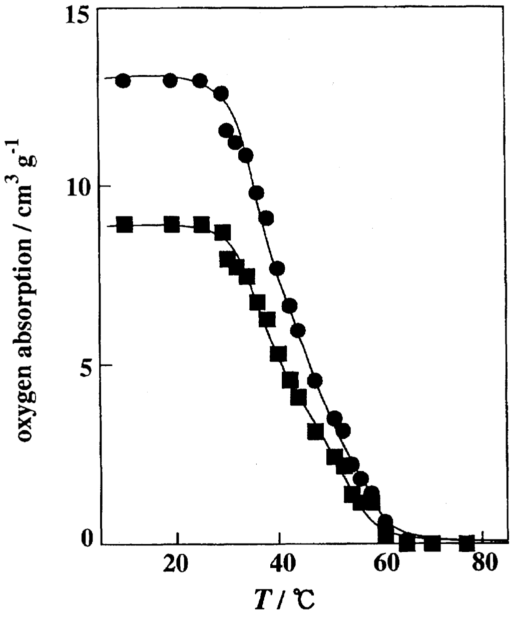

Fig. 2. Effect of temperature on oxygen absorption for the CoP–TIm complex in the solid state (●) and for the CoP/carbon disk (CoP–TIm content = 63%) (■).

Table 2. Electrical Resistance (*R*) and Temperature Elevation upon the Appication of 1.5 V to the CoP/Carbon Disk (Diameter 2 cm×2 mm) (Room Temp = 25 °C)

CoP wt%	*R* Ω	Temp °C
100	∞	25
85	95	25
70	10	38
65	6	46
63	4	66
60	2	95

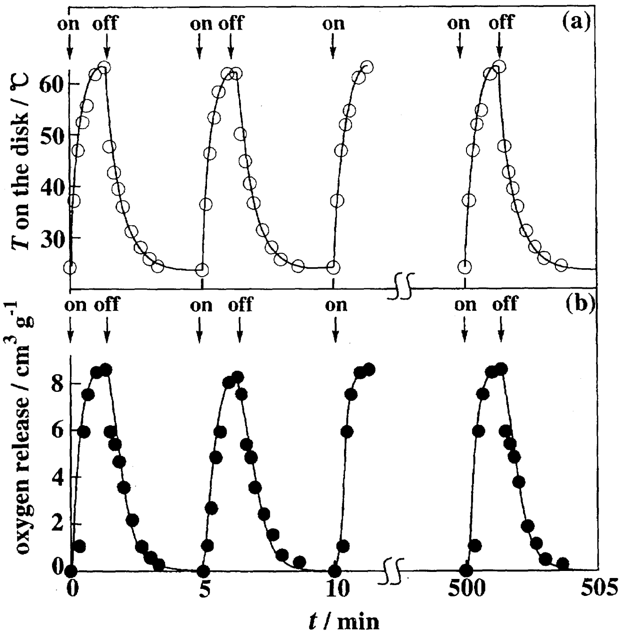

Fig. 3. Temperature-elevation and -depression cycle (a) and oxygen-releasing and -absorbing cycle (b) for the CoP/carbon disk (CoP–TIm content = 63%) in response to 1.5 V-application on and off at 25 °C.

cessively high electric resistance, the disks containing ca. 60% CoP–TIm possessed moderate conductivity enabling them to have a temperature increase while maintaining the CoP–TIm or oxygen absorption capability. The disk containing 63% CoP–TIm exhibited an electrical resistance of 4 Ω and a temperature elevation of 65 °C with an applied voltage of 1.5 V.

The steady-state temperature of the 63% CoP–TIm/carbon disk increased with the application of 1.5 V and reached 65 °C within 1.5 min. In response to the temperature elevation, the disk released oxygen at the 9.0 cm^3 oxygen per gram of composite or 3.6 cm^3 per disk (diameter 2 cm×2 mm). This result coincided with the absorption amount of oxygen into the CoP–TIm powder measured using the thermostat apparatus under the constant volume mentioned above.

Visible reflectance spectra of the CoP–TIm/carbon disk were measured both with and without an applied voltage. The spectrum was broaden but its $\lambda_{\max}$ was changed from ca. 530 nm to ca. 545 nm with the 1.5 V-application. The spectral change was reversible in response to the voltage application, which supported oxygen adduct formation by CoP–TIm in the disk.

Figure 3 shows the temperature-elevation and -depression cycle (a) and the oxygen-releasing and -absorbing cycle (b) for the 63% CoP–TIm/carbon composite disk. The temperature elevation and the corresponding oxygen-releasing were completed within 1.5 min, and the depression and the corresponding oxygen-absorbing took 3 min. The oxygen absorption reaction onto the CoP–TIm powder was rapid and completed within one minute, as mentioned above; this indicated that the heat elevation and cooling of the composite was rate-determining in this experiment and that the response time would be shortened by shaping of the composite. In any case, the oxygen-releasing and -absorbing cycle could be repeated more than 100 times with a 5-min switching on-off interval under ambient conditions.

The CoP–TIm/carbon composite is solvent-free, easily handled, and light by weight; these characteristics besides the oxygen-absorbing and -releasing capability are favorable for testing it as a device to separate oxygen from air and an oxygen-releasing device in response to a 1.5 V-application.

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