Macromolecules **2000,** *33,* 2530−2534

Membranes of the Picket Fence Cobalt Porphyrin Complexed with Poly(vinylimidazole and -pyridine)s: Selective Optical Response to Oxygen

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Received October 26, 1999; Revised Manuscript Received February 7, 2000

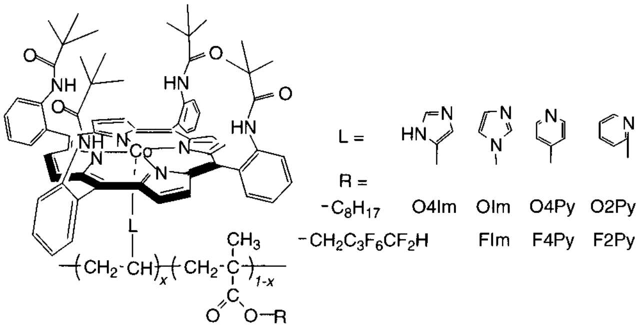
ABSTRACT: Red-colored and solvent-free membranes based on the picket fence cobaltporphyrin (CoP) complexed with two or three kinds of polymer−ligands were prepared, and their visible absorbance responses to oxygen partial pressure were studied. The four CoP complexes with copolymers of 4- and 1-vinylimidazole and 4- and 2-vinylpyridine as a polymer−ligand were characterized by different oxygen affinity: In this order of the copolymers, the oxygen affinity of CoP was decreased by a factor of 10. The membrane composed of the three CoP complexes displayed a selective and continuous response in the visible absorbance ascribed to the oxygen-adduct formation over a wide range of oxygen partial pressure, i.e., 0.01−76 cmHg at atmospheric total pressure. On the other hand, the membrane composed of the two complexes with strong and weak affinity responded in a stepwise manner to oxygen partial pressure. The CoP complexed with and fixed in the polymer−ligands could form an oxygen adduct rapidly and reversibly just as the CoP complex did in a solution. The oxygen response rate of the membrane was shortened inversely with the square root of its thickness. The operational lifetime was longer than 1 month, which was much prolonged for the CoP complexed with the fluoroalkyl methacrylate copolymers: The latter also displayed a selective and reversible oxygen response in water.

Introduction

Chemical sensors selectively responding to oxygen in gas and aqueous samples are known:[1] conductivity measurements with ceramics or metal oxides to detect adsorbed oxygen from gas phases, and electrochemical methods to measure the reduction current of oxygen in aqueous solutions. Several optical sensors have also been introduced that selectively respond to oxygen; the most frequently used devices are based on fluorescence quenching of organic dyes with oxygen.[2] However, the photochemical decomposition of the dyes is their major handicap. A calorimetric oxygen sensor has been tested using hemoglobin solution[3] which, however, suffers from poor chemical stability and from the need for a pH-buffered aqueous solution.

During the past 10 years, the authors have been studying metalloporphyrins as an efficient oxygen carrier and applying them to an oxygen absorbent,[4] an artificial hemoglobin,[5] and oxygen-permselective membranes.[6] Among them, the authors have developed thin, solvent-free membranes of picket fence cobaltporphyrin, (*meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrinato)cobalt(II) (CoP), complexed with an imidazolyl residue of 1-vinylimidazole polymers.[7] Picket fence cobaltporphyrin[8] (CoP, Chart 1) has four pivalamido groups one one side of the plane to provide a cavity for oxygen binding and leaves the other side for complexing with a nitrogenous ligand to improve the oxygen-binding affinity. The CoP in the membrane binds oxygen spectifically, rapidly, and reversibly from air and forms an oxygen adduct. The CoP acts as a fixed carrier of oxygen and facilitates the transport of oxygen in the membrane to display oxygen permselectivity. The CoP membranes are also characterized by a deep red color, and the oxygen-adduct formation is accompanied by a sharp deoxy−oxy spectral change with isosbestic points.[9] Pretsch et al. and the authors have reported[10] in a collaboration that the membranes composed of the CoP−poly(octyl methacrylate-*co*-1-vinylimidazole) complexes serve as a new type of oxygen-sensitive components for optical sensors. In this paper, the authors have succeeded in preparing CoP membranes composed of three different polymer−ligands (Chart 1) by taking into account the ligating equilibrium constants: The useful oxygen-response range was significantly extended, and the operational lifetime was extremely prolonged for the prepared CoP membranes.

Chart 1



Experimental Section

Materials. (*meso*-α,α,α,α-Tetrakis(*o*-pivalamidophenyl)porphyrinato)cobalt(II) (CoP) was synthesized as described in the literature.[8] 4-Vinylimidazole was synthesized from urocanic acid as in the literature.[8] 2,2,3,3,4,4,5,5-Octafluoropentyl methacrylate was prepared by reacting equimolar amounts of methacryloyl chloride and 2,2,3,3,4,4,5,5-octafluoro-1-pentanol (Tokyo Kasei Co.) in the presence of a large excess of triethylamine and purified by distillation (bp 45 °C/3 mmHg). The other vinyl monomers were purchased from Tokyo Kasei Co. and purified by distillation.

Polymer−ligands were prepared by the radical copolymerization of 4-vinylimidazole, 1-vinylimidazole, 4-vinylpyridine,

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10.1021/ma9917949 CCC: $19.00

Table 1. Characterization of the Polymer−Ligands

polymer−ligand	Im or Py[a] content, mol %	$\bar{M}_w$, 10^5	T_g,[b] °C	T_g,[c] °C
O4Im	47	1.2	66	70
Olm	30	1.3	74	76
O4Py	31	1.5	62	67
O2Py	32	1.5	70	72
FIm	31	0.9	55	62
F4Py	48	1.0	61	64
F2Py	49	1.1	58	60

[a] Vinylimidazole or vinylpyridine residue. [b] Glass transition temperature of the polymer−ligand. [c] T_g of the polymer−ligand complexed with 2 wt % CoP.

Table 2. Ligating Equilibrium Constant of CoP in a Solution, Oxygen Affinity, and Enthalpy and Entropy Changes for the Oxygen Adduct Formation for CoP in the Membranes

polymer−ligand	K_L, $10^4 M^{-1}$	p_{50}, cmHg	ΔH, kcal mol^{-1}	ΔS, eu
O4Im	18[a]	2.0	−14	−17
OIm	9.6[a]	7.4	−14	−28
O4Py	8.6[a]	16	−13	−31
O2Py	7.1[a]	25	−13	−34
FIm	13[b]	11	−12	−24
F4Py	7.8[b]	21	−12	−30
F2Py	2.1[c]	64	−12	−39

[a] In toluene. [b] In THF. [c] In toluene/THF (1/1).

or 2-vinylpyridine with octyl methacrylate or 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate using azobis(isobutyronitrile) as the radical initiator. The fraction of the vinylimidazole or vinylpyridine in the total monomer was 40 mol % for all polymerizations. Azobis(isobutyronitrile) concentration was 0.1 and 0.2 wt % for the copolymerization of octyl methacrylate and of octafluoropentyl methacrylate, respectively. Toluene, toluene−ethanol (1/1), or DMF−THF (1/1) was used as the solvent for the copolymerization of vinylimidazole with octyl methacrylate, of vinylpyridine with octyl methacrylate, or of vinylimidazole and -pyridine with octafluoropentyl methacrylate, respectively. A typical example of the copolymerization is as follows. Octafluoropentyl methacrylate (9 mL, 0.03 mol), 4-vinylpyridine (2 mL, 0.02 mol), and azobis(isobutylonitrile) (20 mg) were added to DMF−THF (vol 1/1, 24 mL) under nitrogen. The reaction mixture was heated to 75 °C for 5 h. The mixture was poured into methanol, and the precipitate was purified by reprecipitation twice from acetone to methanol to yield a white powder (yield: 5.3 g, 48%). The vinylpyridine content and the molecular weight of the copolymer were determined to be 48 mol % and 1.0×10^5 by elemental analysis and GPC, respectively. The vinylimidazole or vinylpyridine content and the molecular weight of the copolymers are listed in Table 1.

Membrane Preparation. A chloroform solution of CoP was mixed with a chloroform solution of the octyl methacrylate copolymers (or an acetone solution of CoP and the octafluoropentyl methacrylate copolymers), under a nitrogen atmosphere to complex the imidazolyl or pyridyl residue of the copolymer with the fifth coordination site of CoP (Chart 1). The feed ratios of the polymer−ligands to CoP were calculated based on the ligating equilibrium constants. The solution was cast on a glass plate under an oxygen-free atmosphere, followed by drying in vacuo, to produce a deeply red-colored membrane with a thickness of 1−30 μm. A typical example is as follows. The chloroform solution of CoP (35 μg) was added to the chloroform solution of O4Im (0.40 mg), OIm (1.5 mg), and O2Py (1.9 mg) under a nitrogen atmosphere and cast on a glass plate (1 × 2 cm) followed by drying in vacuo to give a deeply red-colored CoP−(OIm/O4Py/O2Py) membrane with a thickness of 10 μm.

Spectroscopic Measurements. Visible absorption spectra of the CoP membranes and the absorbance ascribed to the oxygen adduct were measured using a UV spectrophotometer (JASCO, V-550). The membrane prepared on the glass plate was set in a cell in the spectrophotometer; the cell was connected to the gas mixing device and an outlet. One side of the membane was left in contact with the measuring gas.

The oxygen-adduct formation kinetics for CoP in the membranes (prepared on a quartz plate) were studied with a pulsed laser-flash spectrophotometer (UNISOKU, TSP-601). Monitoring wavelengths of 413 and 428 nm were selected, which agreed with the maxima of the deoxy− and oxy−CoP, respectively. Formation and dissociation rate constants of the oxygen adduct were calculated by a pseudo-first-order kinetic analysis of the time course of these absorbances.

Other Measurements. The molecular weight of the copolymers was measured with a TOSOH LS-8000 molecular weight analyzer. The glass transition temperatures (T_g) of the copolymers and the CoP membranes were estimated by differential scanning calorimetry (Seiko, DSC 5200). The contact angles (θ) of ultrapure water on the CoP−(OIm/O4Py/O2Py) and CoP−FIm membranes were measured with a contact angle Erma goniometer on 10 different spots of the surface, with the reading being constant for more than 10 min.

Results and Discussion

Complexation of CoP with Polymer−Ligands. CoP yields the five-coordinated CoP−L as shown in Chart 1 in a solution with an excess of an imidazolyl or pyridyl residue (L) of a polymer−ligand. The ligating equilibrium constant of L to CoP (K_L in eq 1) was

$$\mathrm{CoP} + \mathrm{L} \overset{K_L}{\rightleftharpoons} \mathrm{CoP{-}L} \tag{1}$$

estimated by spectroscopic titration of CoP with seven polymer−ligands (listed in Chart 1) in the same solvent used for the following membrane preparation. The visible absorption spectrum of CoP with $\lambda_{max} = 524$ nm changed with the addition of the polymer−ligand to the spectrum with $\lambda_{max} = 527$ nm assigned to a five-coordinated CoP. The spectrum of the CoP−L complex had no shoulder absorption ascribed to a six-coordinated CoP complex even after a large excess addition of the polymer−ligand: CoP predominantly forms the five-coordinated CoP−L complex with the capability of oxygen-adduct formation to give the K_L values summarized in Table 2.

The K_L values for the polymer−ligands were large enough to preferentially form CoP−L in the presence of an appropriate excess of the polymer−ligand for CoP. The K_L values for the imidazole copolymers were larger than those for the pyridine copolymers; the different K_L values mean a competitive equilibrium for the polymer−ligands to prepare a membrane composed of the CoP−L complexes of plural polymer−ligands. By taking into account K_L, the feed ratio of the polymer−ligands to CoP was given: For example, the CoP−(O4Im/OIm/O2Py) membrane was prepared by mixing the three polymer−ligands with CoP under the feed molar ratio of CoP:O4Im:OIm:O2Py = 1:10:20:27). The mixed solution was cast on a glass plate and followed by slow concentration and drying in vacuo. The absorbance of the membrane at 527 nm ascribed to CoP−L ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1} for all the polymer−ligands) supported the complete formation of the CoP−L complexes in the membrane.

Reversible Oxygen-Adduct Formation and Visible Absorbance. The deeply red-colored CoP membrane reversibly exhibited a visible absorption spectral change between the deoxy ($\lambda_{max} = 527$ nm) and the oxy spectrum ($\lambda_{max} = 548$ nm) with clear isosbestic points at 480, 536, and 660 nm, in response to the partial oxygen pressure of the atmosphere (Inset of Figure 1). The spectral change is attributed to the rapid and

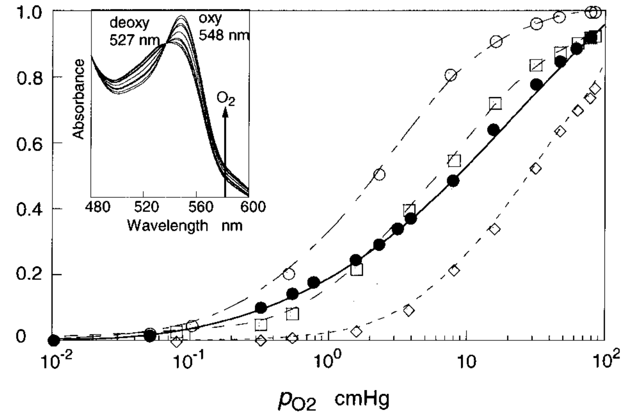

Figure 1. Oxygen response in the absorbance at 547 nm for CoP−(O4Im/OIm/O2Py) (●: $A_{\min} = 0.005 \pm 0.001$; $A_{\max} = 0.924 \pm 0.003$; $N = 12$), −O4Im (○), −OIm (□), and −O2Py (◇) membranes. Inset: Visible absorption spectral change at different partial oxygen pressure (p_{O2}) from 0 to 76 cmHg for the CoP−(O4Im/OIm/O2Py) membrane.

reversible oxygen-adduct formation of the CoP in the membrane. The oxygen-response behavior was monitored at the absorbance ascribed to the oxy form at 548 nm ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}: ϵ of the oxygen-adduct of CoP−L was not influenced by the L species used in this experiment).

The equilibrium curves of the oxygen-adduct formation were drawn based on the absorbance at 548 nm from the oxygen partial pressure (p_{O_2}) of 0 to p_{O_2} of 76 cmHg, for the membranes of CoP complexed with each individual polymer−ligand (Figure 1). The curves obeyed Langmuir's isotherm, and the 50%-saturation points gave the

$$\mathrm{CoP{-}L} + \mathrm{O_2} \overset{1/p_{50}}{\rightleftharpoons} \mathrm{O_2{-}CoP{-}L} \tag{2}$$

oxygen-affinity p_{50} (the oxygen partial pressure at 50% of the oxygen-adduct formation of CoP−L) for the membranes summarized in Table 2. The four (or three) CoP complexes with the copolymers of 4- and 1-vinylimidazole and 4- and 2-vinylpyridine as polymer−ligands were characterized by different oxygen affinities: The affinity was decreased by more than 10 times in the order O4Im > OIm > O4Py > O2Py for the octyl methacrylate copolymers and decreased in the same order FIm > F4Py > F2Py for the octafluoropentyl methacrylate copolymers. This order of the oxygen-affinity of CoP−L nearly agreed with the previously discussed relation between the affinity and the basicity of nitrogenous ligands ligated to CoP (here L).[12]

Figure 1 shows the oxygen-response behavior, i.e., the degree of absorbance change at 547 nm (Δ*A*) vs logarithmic oxygen partial pressure in the atmosphere, for three CoP membranes composed of the CoP complexed with O4Im, OIm, and O2Py, which are characterized by a 10-fold difference in oxygen-affinities in the order O4Im > OIm > O2Py. Figure 1 also shows the oxygen-response curve for the CoP−(O4Im/OIm/O2Py) membrane: The response curve nearly agreed with that calculated by the simple addition of the individual curves for three O4Im, OIm, and O2Py moieties. That is, the CoP−(O4Im/OIm/O2Py) membrane displayed an absorbance increase at both extremely low and high oxygen partial pressures due to the strong and weak oxygen affinity of the CoP−O4Im and −O2Py complex, respectively, and its useful response window was extended to 0.01−76 cmHg of oxygen partial pressure by the combination of the three different polymer−ligands.

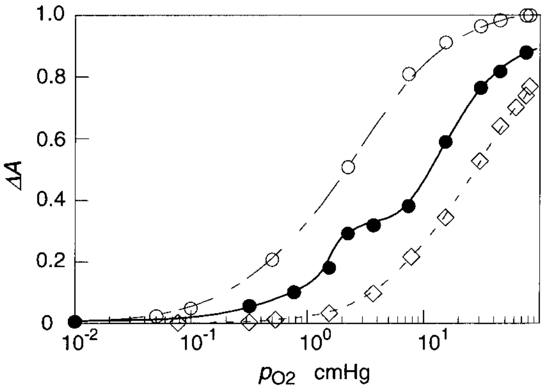

Figure 2. Oxygen response in the absorbance at 547 nm for the CoP−(O4Im/O2Py) (●: $A_{\min} = 0.005 \pm 0.001$; $A_{\max} = 0.880 \pm 0.006$; $N = 8$), −O4Im (○), and −O2Py (◇) membranes.

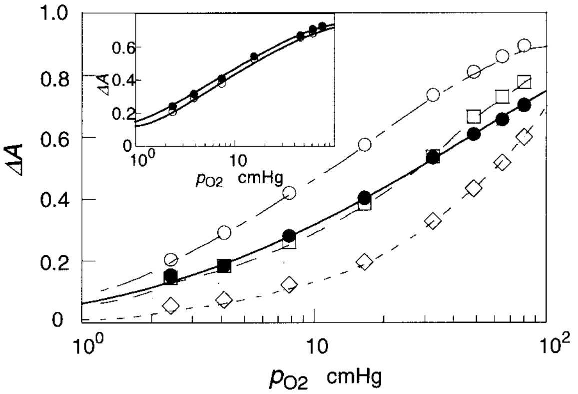

Figure 3. Oxygen response in the absorbance at 547 nm for the CoP−(FIm/F4Py/F2Py) (●: $A_{\min} = 0.139 \pm 0.002$; $A_{\max} = 0.686 \pm 0.005$; $N = 8$), −FIm (○), −F4Py (□), and −F2Py (◇) membranes. Inset: Response observed 1 day (●) and 2 months (○) after membrane preparation.

On the other hand, Figure 2 shows the response curve for the CoP−(O4Im/O2Py) membrane which lacked CoP−OIm with an intermediate affinity, in contrast to the CoP−(O4Im/OIm/O2Py) membrane. The response curve showed a stepwise shape.

The oxygen-response curves for the membranes of the fluoropentyl methacrylate copolymers CoP−FIm, CoP−F4Py, CoP−F2Py, and CoP−(FIm/F4Py/F2Py) are shown in Figure 3. The oxygen affinities of the CoP complexed with the fluorocopolymer−ligands were smaller than those of the corresponding octylmethacrylrate copolymer−ligands (see Table 2), probably because of the rigidity of the fluorocopolymer−ligands. Anyway, the response curves were shifted somewhat to a higher oxygen partial pressure area, but the response curve of the CoP−(FIm/F4Py/F2Py) membrane still covered the oxygen partial pressure range of 0.1−76 cmHg.

Oxygen-Adduct Formation of the CoP Fixed in the Membranes. Enthalpy and entropy change (Δ*H* and Δ*S*) for the oxygen-adduct formation of the CoP complexes in the membrane state were estimated from the temperature dependency of p_{50}, i.e., the ln p_{50} −1/*T* van't Hoff plots, and are also given in Table 2. The Δ*H* values of CoP complexes, i.e., the temperature dependencies of the oxygen affinity, were almost the same for the seven CoP membranes. The oxygen-adduct formation is an exothermic reaction (a negative Δ*H* value) and the oxygen affinity decreases with temperature; how-

Table 3. Formation and Dissociation Rate Constants for the Oxygen Adduct of CoP Complexed with the Polymer−Ligands at 25 °C

polymer−ligand	state[a]	k_D,[b] 10^{-2} cm^3(STP) cm^{-3}cmHg	p_{50}, cmHg^{-1}	k_{on}, 10^7 M^{-1} s^{-1}	k_{off}, 10^4 s^{-1}
OIm	membr	0.85	7.4	3.8	9.8
FIm	membr	1.6	11	0.16	1.2
MeIm[c]	in tol	0.16	14	1.2	1.2
OIm	in tol	0.16	20	2.0	2.7

[a] In solid membrane state (membr) or in toluene (tol) solution. [b] Physical oxygen solubility coefficient in the polymer membrane or in toluene. [c] MeIm: *N*-methylimidazole.

ever, its tendency was not significantly affected by the polymer−ligand species ligated with CoP, and deviations of the oxygen-response curve with temperature could be corrected by the van't Hoff type temperature dependency of p_{50} or the ΔH values.

The photodissociation and recombination of oxygen from and to the CoP complexed with the polymer−ligand in the solid membrane state were observed in situ by pulse and laser flash photolysis spectroscopy. The formation and dissociation rate constants of the oxygen-adduct of CoP (k_{on} and k_{off} in eq 3) were estimated using

$$\mathrm{L{-}CoP{-}O_2} \xrightarrow{h\nu} \mathrm{L{-}CoP} + \mathrm{O_2} \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} \mathrm{L{-}CoP{-}O_2} \quad (3)$$

pseudo-first-order kinetics for the spectral time courses in the oxygen recombination and are also given in Table 3. The k_{on} and k_{off} values of the CoPs complexed with the polymer−ligands, CoP−OIm and CoP−FIm, in the solid or solvent-free membrane state were similar to those of the corresponding CoP complex in toluene solution. This means that the CoP complexed with the polymer−ligands is kinetically active for oxygen-adduct formation even in the membrane and responds to oxygen rapidly and reversibly.

Response Rate Constant of the Membranes. The absorbance change of the CoP membranes in response to oxygen partial pressure in the atmosphere was very rapid. The oxygen response rate constant (k'_{on}) was estimated by analyzing the time courses of the absorbance change after exposure of the membrane to the mixed gases of different oxygen partial pressure. They were analyzed based on the pseudo-first-order kinetics of the Langmuir isotherms, and the examples for the CoP−(OIm/O4Py/O2Py) membrane are plotted in Figure 4. The response rate constant was shortened inversely with the square root of the membrane thickness in Figure 4. This means that the response rate is diffusion controlled for oxygen in the membrane, which agrees with the very rapid reaction of CoP with oxygen mentioned above. An immediate (millisecond) response is expected for a very thin CoP membrane with a thickness of 0.1 μm.

Operational Lifetime. The inset in Figure 3 shows the response curve for the CoP−(FIm/F4Py/F2Py) membrane after exposure of the membrane to laboratory air for 2 months. The membrane exhibited a fairly stable response for more than 1 month.

The half-lifetime (τ) of the CoP complexed with the polymer−ligands was measured by allowing the membrane to stand in a laboratory air and in water with room temperature. The Co^{II}P−L complex with the capability of the oxygen-adduct formation was slowly decreased via its irreversible oxidation to the Co^{III}P−L without the oxygen-response capability, which was monitored by the visible absorption at $\lambda_{max} = 549$ nm. The decreased time course of the active Co^{II}P complex approximately followed first-order kinetics with τ values listed in Table 4. The τ values were significantly long, especially for the fluorinated membrane CoP−(FIm/F4Py/F2Py). It has been concluded that the major process of the irreversible oxidation of Co^{III}P during its oxygen-adduct formation is a proton-driven oxidation caused by the attack of a water or a protic molecule (eq 4).[6] The contact angle of a water droplet on the

$$\mathrm{L{-}CoP{-}O_2} + \mathrm{H^+(H_2O)} \rightarrow \mathrm{L{-}Co^{III}P{-}OH^-} + \mathrm{HO_2}^* \quad (4)$$

membranes (Table 4) indicates that the CoP membrane composed of the fluoromethacrylate CoP polymers is more water-repellent. The hydrophobic property of the membrane is considered to suppress the irreversible

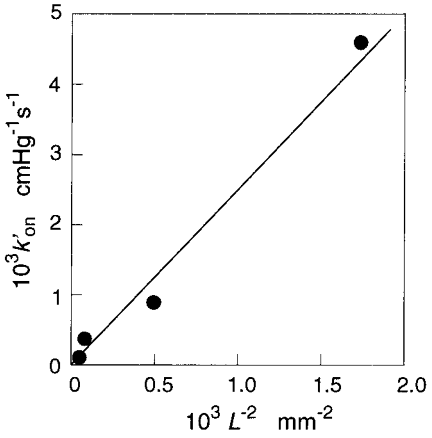

Figure 4. Response rate constant (k'_{on}) vs membrane thickness (L) for the CoP−(OIm/O4Py/O2Py) membrane.

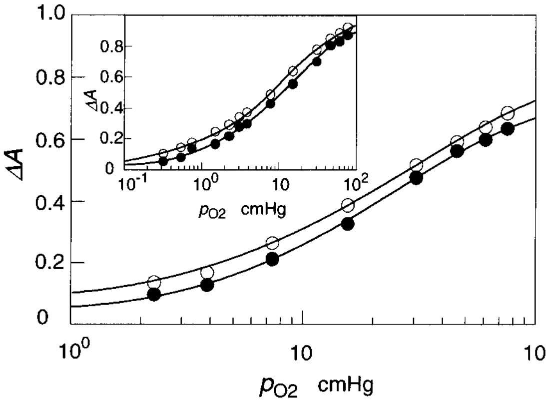

Figure 5. Oxygen response in the absorbance at 547 nm for the CoP−(FIm/F4Py/F2Py) membrane in water (●) and in O_2/N_2 mixture gases (○). Inset: Response (●) observed after 1 month in water.

Table 4. Half-Lifetime (τ) of and the Contact Angle of a Water Droplet on the CoP Membranes

polymer−ligand	τ, days in air[a]	τ, days in water[b]	contact angle, deg
OIm/O4Py/O2Py	48	13	76
FIm/F4Py/F2Py	99_9	46_1	91

[a] Exposed to laboratory air at 25 °C (in dry air, τ > 3 months for the CoP−(OIm/O4Py/O2Py) membrane). [b] Dipped in distilled water in an open vessel at 25 °C.

oxidation of CoP caused by the water molecule and to prolong the operational lifetime of the CoP membrane.

Response to Oxygen Dissolved in an Aqueous Solution. Because the lifetime of the CoP membrane was not short even when standing in water, the response to oxygen dissolved in an aqueous solution was examined. The oxygen-response curves of the CoP membranes were nearly similar to those to oxygen in O_2/N_2 mixture gases: a slight decrease in the absorbance change is probably because the lower physical solubility of oxygen in water reduces the amount of oxygen dissolved in the membrane. Anyway, after the correction of such a decrease, the fluorinated membrane of CoP seems to be appropriate to determine dissolved oxygen in aqueous solutions.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research in Priority Area (No. 11136248 “Metal-assembled Complexes”) from the Ministry of Education, Science, Sports, and Culture, Japan, and by the Materials Research Laboratory for Bioscience and Photonics, Waseda University. The authors thank Prof. E. Pretsch (Swiss Federal Institute of Technology) for his productive comments on this study.

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MA9917949