

A Study of Cobalt(II) Porphyrins on Their Oxygen-Binding Behaviors and Oxygen-Facilitated Transport Properties in Polymeric Membranes

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The oxygen-binding behaviors of five cobalt(II) *meso*-tetrakis(substituted phenyl)porphyrin complexes [CoTPP, CoT(2-Cl)PP, CoT(4-Cl)PP, CoT(4-MeO)PP, and CoT(2,4-2MeO)PP] in chloroform solution were investigated using a UV–visible spectrophotometer. It shows that the substituents and the fifth ligand in the cobalt(II) porphyrins strongly influence the oxygen-binding rate. The cobalt(II) porphyrin complexes substituted with an electron-donating group on the *meso*-phenyl ring increase the oxygen-binding rate, in contrast, the cobalt(II) porphyrin complexes substituted with an electron-accepting group decrease the oxygen-binding rate; as fifth ligand, both imidazole and pyridine enhance the oxygen-binding rate of cobalt porphyrin complexes, and the imidazole has a higher oxygen-binding rate. Meanwhile, the oxygen-facilitated transport properties in ethyl cellulose (EC) membranes containing five cobalt porphyrins as oxygen carriers were studied, too. The oxygen-facilitated transport in a membrane containing such complexes could be strongly affected by the different substituents and fifth ligand of the complexes.

Introduction

Scholander found that the existence of hemoglobin could improve the oxygen transport in solution in 1960.^{1,2} Since that time, the oxygen transport through a polymer membrane containing transition metal complexes as oxygen carriers has been widely investigated,^{3–5} because the addition of oxygen carriers in a membrane can increase the oxygen permeability and oxygen/nitrogen selectivity simultaneously.^{6,7} On the other hand, the oxygen-enriched properties of those polymeric membranes are related to the oxygen-binding behaviors of the oxygen carriers, but only few systematic studies about the influences of the oxygen carrier structures on their oxygen-binding behaviors and oxygen-enriched properties have been reported in the literature.

In our research group, a series of cobalt Schiff base complexes as oxygen carriers have been synthesized, and the facilitated transport of molecular oxygen in the polymeric membranes containing those complexes as

oxygen carriers has been investigated.^{8–10}

In this paper, five cobalt(II) *meso*-tetrakis(substituted phenyl)porphyrin complexes as oxygen carriers were synthesized, in which the substituents were varied from an electron-donating group to an electron-accepting group. The influences of the substituted groups and the fifth ligands in the oxygen carriers on the oxygen-binding rate in chloroform solution and the oxygen-facilitated transport in polymeric membranes containing these complexes were studied.

Experimental Section

Synthesis of Oxygen Carriers. Five cobalt(II) *meso*-tetrakis(substituted phenyl)porphyrins [CoTPP, CoT(2-Cl)PP, CoT(4-Cl)PP, CoT(4-MeO)PP and CoT(2,4-2MeO)PP] were synthesized as reported in the literature.^{11,12} The structures of these five complexes are shown in Scheme 1.

Anal. Calcd for CoTPP: C, 78.68; H, 4.20; N, 8.34. Found: C, 78.49, 78.61; H, 4.14, 4.17; N, 8.37, 8.48. ¹H NMR (CDCl₃, 400 MHz): δ 9.73–9.93 (12 H); δ 13.14 (8 H); δ 15.89–15.93 (8 H). Anal. Calcd for CoT(2-Cl)PP: C, 65.29; H, 2.99; N, 6.92. Found: C, 65.14, 64.80; H, 2.64, 2.65; N, 6.51, 6.54. ¹H NMR

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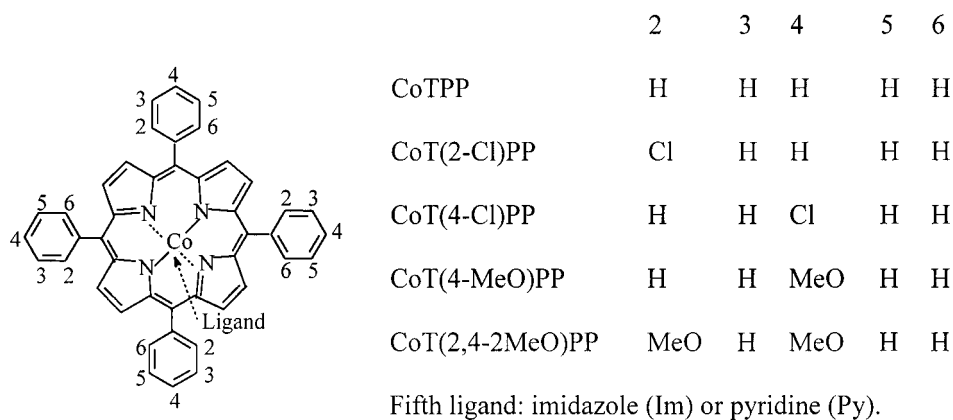
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Scheme 1. Structures of Five Cobalt(II) Porphyrins^a

^aCoTPP, cobalt(II) *meso*-tetraphenylporphyrin; CoT(2-Cl)PP, cobalt(II) *meso*-tetrakis(2-chlorophenyl)porphyrin; CoT(4-Cl)PP, cobalt(II) *meso*-tetrakis(4-chlorophenyl)porphyrin; CoT(4-MeO)PP, cobalt(II) *meso*-tetrakis(4-methoxyphenyl)porphyrin; CoT(2,4-2MeO)PP, cobalt(II) *meso*-tetrakis(2,4-dimethoxyphenyl)porphyrin.

(CDCl₃, 400 MHz): δ 9.15–9.80 (12 H); δ 11.97–12.55 (4 H); δ 14.85–15.47 (8 H). Anal. Calcd for CoT(4-Cl)PP: C, 65.29; H, 2.99; N, 6.92. Found: C, 65.24, 65.31; H, 3.16, 3.02; N, 6.60, 6.33. ¹H NMR (CDCl₃, 400 MHz): δ 9.88–9.92 (8 H); δ 12.96–12.97 (8 H); δ 15.80 (8 H). Anal. Calcd for CoT(4-MeO)PP: C, 72.82; H, 4.58; N, 7.08. Found: C, 72.93, 73.14; H, 4.58, 4.75; N, 7.16, 7.14. ¹H NMR (CDCl₃, 400 MHz): δ 5.22 (12 H); δ 9.41 (8 H); δ 13.12 (8 H); δ 15.93 (8 H). Anal. Calcd for CoT(2,4-2MeO)PP: C, 68.49; H, 4.86; N, 6.14. Found: C, 68.66, 68.74; H, 4.89, 4.92; N, 6.11, 6.45. ¹H NMR (CDCl₃, 400 MHz): δ 3.41–3.92 (12 H); δ 5.16 (12 H); δ 8.74–8.95 (8 H); δ 12.18–12.31 (4 H); δ 15.41–15.66 (8 H).

Spectroscopic Measurements. The spectral changes of different complexes in chloroform solution were observed using a Shimadzu UV-240 spectrophotometer. At first the chloroform was bubbled with nitrogen for 1 h, then the cobalt porphyrin complex (CoPor) was dissolved in the chloroform under nitrogen with the concentration of approximately 1×10^{-5} M. The ligand [imidazole (Im) or pyridine (Py)] with a mole ratio of 1:1 (to the cobalt porphyrin) was added into the chloroform solution under nitrogen to form cobalt porphyrin/ligand chloroform solution (CoPorIm or CoPorPy). The cell with this complex solution was immediately mounted in the cell compartment of the spectrophotometer. The UV-visible absorption spectra of those chloroform solutions were measured at different oxygen-exposure time intervals.

Membrane Preparation. The cobalt porphyrins were complexed with imidazole or pyridine in chloroform to form CoPorIm or CoPorPy complexes, then the chloroform solution of CoPorIm or CoPorPy was mixed with a chloroform solution of ethyl cellulose (EC, with ethoxy content of 45.9%, density of 1.14 g/cm³ determined from the density gradient tube method using a H₂O/CaCl₂ mixture system at 303 K) and carefully cast on a Teflon plate in a vacuum to form a transparent, red membrane with a thickness of about 55 μ m.

Permeation Measurement. Gas permeability under various upstream gas pressures was measured using a low-vacuum permeation apparatus with a stable thermostat (Rika Seiki Inc. Gas permeation apparatus K-315N), and the temperature was kept at 303 K. The pressures on the upstream and the downstream sides were detected using a Baratron absolute-pressure gauge (MKS Instruments). The permeability was calculated from the slopes of the steady-state straight line of the permeation curves. The experimental error in the gas permeability was estimated to be $\pm 3\%$, the greatest source of error being the membrane thickness. Oxygen permeability P_{O_2} is reported below in unit of barrer, 1 barrer = 10^{-10} cm³ (STP)·cm/(cm²·s·cmHg).

Results and Discussion

Oxygen Binding to the Complexes with Imida-

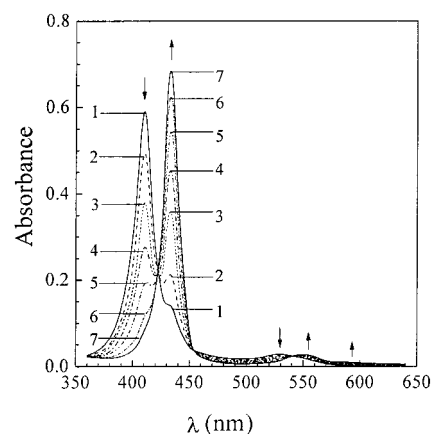


Figure 1. The absorption spectra of Co(TPP)Im in CHCl₃ at different oxygen-exposure times (curves 1–7 corresponded to $t = 0, 10, 30, 60, 110, 170,$ and 270 min, respectively).

zole as Fifth Ligand. Figure 1 shows the absorption spectra of the cobalt porphyrin complex CoTPP with imidazole as fifth ligand [Co(TPP)Im] in chloroform solution at different oxygen-exposure time. It can be found that the absorption peaks of Co(TPP)Im at 410 and 528 nm decrease and the peaks of 433, 550, and 585 nm (very weak) increase with increasing oxygen-exposure time. This means that the peaks of 410 and 528 nm correspond to the absorption of Co(TPP)Im in its deoxygenation state, and the peaks of 433, 550, and 585 nm correspond to the absorption of Co(TPP)Im in its oxygenation state. The absorption peaks of Co(T(4-MeO)PP)Im, Co(T(2,4-2MeO)PP)Im, Co(T(4-Cl)PP)Im, and Co(T(2-Cl)PP)Im in their deoxygenation and oxygenation state are similar to those of Co(TPP)Im and are listed in Table 1.

In the meantime, it can be found from Figure 1, after a certain oxygen-exposure time, namely the critical oxygen-exposure time, the absorption peaks at 410 and 528 nm of Co(TPP)Im in its deoxygenation state could disappear and the absorption peaks at 433, 550, and 585 nm of Co(TPP)Im in its oxygenation state would rise to a maximum. However, the rate of this absorption peak change is different for five cobalt porphyrins with varying substituents. The different critical time for the five complexes (shown in Table 2) reflects the different oxygen-binding rate of the five complexes.

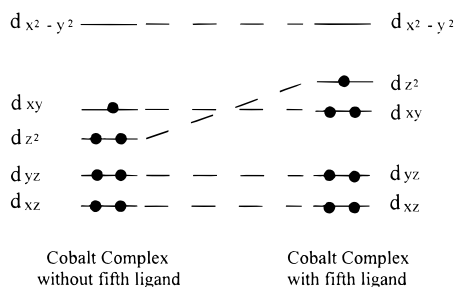
Table 1. Absorption Peaks of Five Cobalt Porphyrin Complexes in Their Deoxygenation and Oxygenation State

complexes	peaks of deoxygenation state (nm) ^a	peaks of oxygenation state (nm) ^a
Co(TPP)Im	410(s) 528(w)	433(s) 550(w) 585(vw)
Co(T(4-MeO)PP)Im	414(s) 531(w)	436(s) 555(w) 595(vw)
Co(T(2,4-2MeO)PP)Im	414(s) 530(w)	435(s) 551(w) 587(vw)
Co(T(4-Cl)PP)Im	411(s) 528(w)	434(s) 550(w) 588(vw)
Co(T(2-Cl)PP)Im	410(s) 528(w)	433(s) 550(w) 585(vw)

^a s = strong; w = weak; vw = very weak.

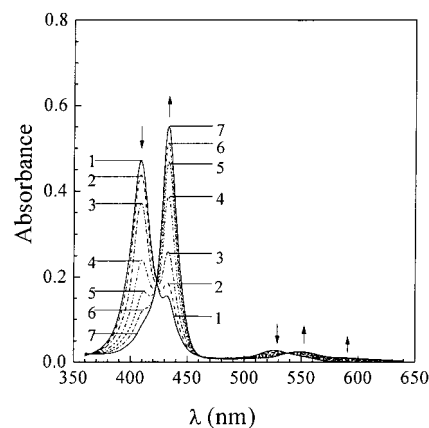
Table 2. Critical Oxygen-Exposure Time for the Five Complexes in Chloroform (min)

fifth ligand	CoT(2,4-2MeO)PP	CoT(4-MeO)PP	CoTPP	CoT(4-Cl)PP	CoT(2-Cl)PP
imidazole	150	210	270	540	610
pyridine	300	480	720	>720	>720

Scheme 2. Energy Level Diagram of a Cobalt Complex with and without the Fifth Ligand^{13,14}

The results in Figure 1 and Table 2 show that the complexes with methoxy group as the substituent on the *meso*-tetrakis(ortho- or para-substituted phenyl)porphyrins [CoT(4-MeO)PP, CoT(2,4-2MeO)PP] have shorter critical time than the complex without any substituent (CoTPP), and the complexes with chloro as the substituent [Co(4-Cl)PP and CoT(2-Cl)PP] have longer critical time than CoTPP. The oxygen-binding rate order of the five complexes with different substituents in phenyl ring is two MeO as substituents > one MeO > H > Cl in the para site > Cl in the ortho site. This indicates that the introduction of an electron-donating group (such as MeO) as substituent in the cobalt complexes could increase the oxygen-binding rate, and the introduction of an electron-accepting group (such as Cl) as substituent could reduce the oxygen-binding rate.

The four-coordinated cobalt complex has a planar structure, in which the unpaired electron of the Co(II) center is in the d_{xy} orbital and the complex has the configuration $(d_{xz})^2(d_{yz})^2(d_{z^2})^2(d_{xy})^1$ (Scheme 2). The binding of an axial fifth ligand could lead to a structure change of the complex from planar to square-pyramidal, raising the d_{z^2} orbital above the d_{xy} orbital, and thus the unpaired electron will occupy the d_{z^2} orbital, resulting in the configuration $(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{z^2})^1$. This latter configuration is a necessary prerequisite of oxygenation, because it is favorable to the approach of oxygen to the cobalt center from the z direction opposite to the axial ligand.^{13,14}

**Figure 2.** The absorption spectra of Co(TPP)Py in CHCl_3 at different oxygen-exposure times (curves 1–7 corresponded to $t = 0, 40, 100, 180, 280, 420,$ and 720 min, respectively).

When oxygen is coordinated to the cobalt porphyrin complex, the sp^2 lone pair on oxygen should be donated to the d_z orbital on the metal to form a σ bond, accompanied there is the formation of a π bond by π back-bonding from the filled d_{xz} (or d_{yz}) orbitals on the metal into the empty π^* orbitals of oxygen.^{13,14} Thus the stability of the oxygen complex is dependent upon the electron-donating ability of the metal to the π^* orbitals of oxygen. The greater electron density on the cobalt ion is more favorable to the π electron donation from metal to oxygen, leading to a more stable formation of oxygenated complex and faster oxygen-binding rate of the complex.

An electron-donating group (such as MeO) in the *meso*-tetrakis(ortho- or para-substituted phenyl)porphyrin ring could increase the electron density on the cobalt ion by its electron-inductive effects through the π conjugated bond in the porphyrin ring, which could enhance the oxygen-binding affinity of the cobalt ion. As a result, the oxygen-binding rate of these complexes to the oxygen would be faster. On the contrary, an electron-accepting group (such as Cl) in the *meso*-tetrakis(ortho- or para-substituted phenyl)porphyrin ring could decrease the electron density on the cobalt ion, leading to a reduction in the interaction between the oxygen and cobalt ion and a decrease in the oxygen-binding rate. And the chloro group in the ortho site has stronger electron-accepting inductive effects than that in the para site, which could decrease the electron density on the central cobalt ion to a greater extent, so the complete oxygenation of CoT(2-Cl)PP could need more time than that of Co(4-Cl)PP.

Oxygen Binding to the Complexes with Pyridine as Fifth Ligand. The absorption spectral changes of CoTPP with pyridine as fifth ligand (Co(TPP)Py) in chloroform solution were also investigated under the same experimental conditions as shown in Figure 2. It can be seen that the peaks at 410 and 528 nm corresponding to the absorption of Co(TPP)Py in its deoxygenation state decrease, and the peaks at 433, 550, and 585 nm corresponding to the absorption of Co(TPP)Py in its oxygenation state increase with increasing the oxygen-exposure time. The absorption peaks of all the five complexes with pyridine as fifth ligand are similar, but they have longer critical oxygen-exposure time than the same complexes with imidazole as fifth ligand,

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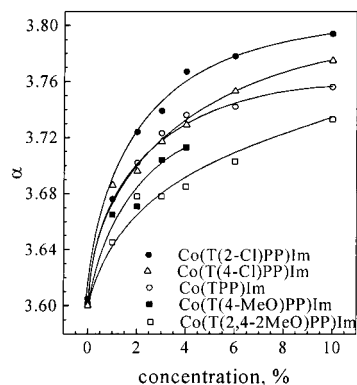


Figure 3. Effect of complex concentration on the α for five EC membranes containing cobalt porphyrins (imidazole as fifth ligand; upstream pressure of 199.39 kPa).

respectively. For example, the critical oxygen-exposure time is 270 min for the complex Co(TPP) with imidazole as fifth ligand, but it is 720 min for the same complex with pyridine as fifth ligand (Table 2).

As discussed above, the increase of the electron density on the metal could increase the oxygen-binding rate of the complex. Imidazole is much better π donor than pyridine, so as a ligand it can increase the electron density on the metal more than pyridine, leading to a faster oxygen-binding rate. This means that the oxygenation behaviors of the cobalt complexes are strongly influenced by their fifth ligand.

Oxygen Facilitated Transport in EC Membranes with Cobalt Porphyrins as Oxygen Carriers. We have studied the oxygen-facilitated transport behaviors of poly(dimethylsiloxane) (PDMS) and EC membranes containing the five cobalt porphyrins as oxygen carriers.^{11,12} It was found that the oxygen permeability and oxygen/nitrogen selectivity (α) of these polymer membranes could be simultaneously enhanced by addition of cobalt porphyrin complexes into the membranes.

Figure 3 shows the effects of oxygen carrier concentration on the α in EC membranes containing cobalt porphyrin complexes as oxygen carriers (with imidazole as fifth ligand; upstream pressure of 199.39 kPa).

Generally, with the increase of complex concentration in EC membranes, the oxygen/nitrogen selectivity was increased and influenced by the complex structures. At the same complex concentration and experimental conditions, the selectivity of EC membranes containing the complexes with methoxy group as the substituent on the *meso*-tetrakis(ortho- or para-substituted phenyl)porphyrins [CoT(4-MeO)PP, CoT(2,4-2MeO)PP] is lower than for those containing the complex without any substituent (CoTPP), and the selectivity of EC membranes containing complexes with chloro as the substituent in the phenyl para site of porphyrin (CoT(4-Cl)PP) is close to (at lower complex concentration) or higher than for those containing CoTPP at higher complex concentration; meanwhile, the EC membranes containing complexes with chloro as the substituent in the ortho site [CoT(2-Cl)PP, which has longest critical oxygen-exposure time among all complexes with imidazole as ligand, as shown in Table 2] has the highest selectivity among all membranes, which suggests that the addition of porphyrin complexes with an electron-accepting group (such as Cl) in the *meso*-tetrakis(ortho-

Table 3. Oxygen-Enriched Characteristics of EC Membranes at an Upstream Pressure of 8.00 kPa (Complex Concentration of 1.0 wt %)

membrane samples	P _{O₂} barrer	α
EC without complex	9.68	3.55
EC/Co(T(2,4-2MeO)PP)Im	10.75	3.85
EC/Co(T(4-MeO)PP)Im	10.78	3.95
EC/Co(TPP)Im	11.29	4.18
EC/Co(T(4-Cl)PP)Im	11.52	4.22
EC/Co(T(2-Cl)PP)Im	12.39	4.44
EC/Co(T(2-Cl)PP)Py	10.82	3.95

or para-substituted phenyl)porphyrin ring could greatly enhance the oxygen permeation properties in polymeric membranes.

In addition, the oxygen-enriched characteristics of EC membranes containing porphyrin complexes with pyridine as fifth ligand are similar to those with imidazole as fifth ligand, but the EC membranes containing complexes with imidazole have higher selectivity than those with pyridine as fifth ligand. This indicates that the imidazole is a better fifth ligand than pyridine in the porphyrin complexes to improve the oxygen permeation properties in membranes.

These results could become more obvious when the upstream pressure was decreased. Table 3 shows the oxygen-enriched characteristics of EC membranes containing complexes as oxygen carriers at lower upstream pressure (fixed complex concentration of 1.0 wt %). When the upstream pressure of the membranes is reduced to 8.00 kPa, the oxygen permeability P_{O₂} and selectivity in EC membranes containing complexes increased simultaneously; meanwhile, the P_{O₂} and α in EC membrane without any complex changed slightly. And the introduction of Co(T(2-Cl)PP)Im into the EC membranes could enhance the P_{O₂} and α to a greater extent than that of Co(T(2-Cl)PP)Py.

From Figure 3 and Table 3, it can be found that the α of these polymeric membranes containing complexes as oxygen carriers is increased according to the order CoT(2,4-2MeO)PP, CoT(4-MeO)PP, CoTPP, CoT(4-Cl)PP, and CoT(2-Cl)PP under the same experiment conditions, which is consistent with the increasing order of critical oxygen-exposure time of complexes in solution, suggesting that a higher critical oxygen-exposure time of complexes in solution corresponds to a higher oxygen/nitrogen selectivity in membranes containing complexes. And the membranes containing complexes with imidazole as fifth ligand have higher oxygen permeability and oxygen/nitrogen selectivity than those with pyridine as fifth ligand [for example, comparison between Co(T(2-Cl)PP)Im and Co(T(2-Cl)PP)Py]. These results indicate that oxygen-facilitated transport in polymeric membranes could be influenced by the substituent effects of porphyrin complexes and related to the oxygen-binding behaviors of complexes in solution. A more detailed discussion will be given elsewhere.¹⁵

Conclusions

The introduction of an electron-donating group as substituent in the cobalt porphyrin complex could increase the complex oxygen-binding rate; in contrast, the introduction of an electron-accepting group in the

complex could decrease its oxygen-binding rate. Compared to pyridine, imidazole is a better ligand to increase the complex oxygen-binding rate. The oxygen-facilitated transport in a membrane containing such complexes as oxygen carriers could be strongly influenced by the different substituents and the fifth ligand

of the complexes.

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