Oxygen-Carrying Cobaltporphyrin Complexed with Electroconductive Poly(3,4-azopyridylene)

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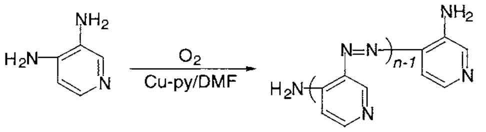
Poly(3,4-azopyridylene) was prepared and complexed with picket-fence coaltporphyrin; the polymer complex displayed both the selective and reversible oxygen-binding and the electroconductivity of 10^{-5} S cm^{-1}.

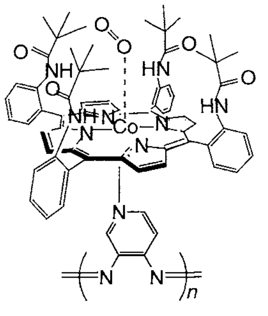
Metalloporphyrin complexes were exhaustively synthesized as oxygen-carrying molecules for the decade before and after 1980.[1-3] A typical example is the complex of *meso*-tetrakis(α, α, α, α-*o*-pivalamidophenyl)porphyrinatocobalt (picket-fence cobaltporphyrin, CoP).[1,4] The CoP complexed with a nitrogeneous ligand such as imidazole and pyridine can selectively, rapidly, and reversibly bind molecular oxygen from air. The CoPs complexed with a solid polymer-ligand acted as a fixed carrier of oxygen, and we have been applying them to an oxygen adsorbent and an oxygen permselective membrane.[5,6] We have also reported an oxygen-releasing device of cobalt complexes, which was prepared as a composite of the oxygen-carrying but electrically insulating cobalt complex and conductive carbon powder and released the adsorbed oxygen in response to a voltage application.[7,8]

On the other hand, much effort has been expended in synthesizing π-conjugated polymers involving ligand moieties to study effects through the conjugated backbone between pendantly coordinated metal complexes or redox sites.[9,10] However, there has been no report on combination of a π-conjugated and electroconductive polymer-ligand and an oxygen-carrying metal complex. We report here, for the first time, the preparation of the cobaltporphyrin CoP complexed with an azopyridine polymer and its oxygen-carrying capability and conductivity.

3,4-Diaminopyridine was polymerized *via* an oxidative polymerization (1) with a Cu-pyridine catalyst under oxygen in DMF at room temperature. Poly(3,4-azopyridylene) (PAP) was obtained as a black powder.[11] The IR peaks at 3395 and 3284 cm^{-1} ascribed to $\nu_{N\text{-}H}$ of the monomer disappeared, and a new absorption at 1543 cm^{-1} for PAP was ascribed to the formation of an azo group ($\nu_{N=H}$). The structure was characterized by ^{1}H-NMR (DMF-d_7): 8.36-5.79(m, 3H, py-H), 5.01(s, 2H, -NH_2). The degree of polymerization was estimated to be 11 (mol. wt. 1.2×10^3) from the ^{1}H-NMR and the colorimetric titration of the terminal amino group.[12] The polymer was hardly soluble in common solvents, except in DMF: The visible absorbance of the solution obeyed the Lambert-Beer's law until the concentration of 5 wt%.



(1)



Scheme 1.

The DMF solution of PAP was mixed with the DMF solution of CoP under nitrogen atmosphere, the new absorption was observed at 530 nm, which was the same as the CoP-pyridine complex and ascribed to the five-coordinated CoP complex (Scheme 1). The five-coordinate structure of CoP with PAP was also confirmed by ESR spectroscopy.[13]

$$\text{CoP} \;+\; \text{O}_2 \; \overset{1/p_{50}}{\rightleftharpoons} \; \text{CoP-O}_2 \qquad (2)$$

The UV/vis absorption spectrum reversibly changed from the deoxy (λ_{max} = 530 nm) and oxy one (λ_{max} = 549 nm) through the isosbestic point (540 nm) in response to partial oxygen pressure. The oxygen-binding affinity or the p_{50} value (partial oxygen pressure to give a half-saturation of the binding site CoP, Eq. 2) of CoP-PAP was determined from the oxygen-binding equilibrium curve which was drawn based on the visible spectral change, and was given in Table 1 with those of the reference complexes. The oxygen affinity was low (large p_{50}) for the PAP complex. The basicity or acidity of PAP was determined with acid-base titration:[14] pK_a = 4.5 (5.4 for pyridine). It has been known that the oxygen affinity of the CoP complex is dependent on the basicity of a ligand;[1-3] the low basicity of the pyridine residue in PAP seems to cause the low oxygen affinity of CoP-PAP. However, it was improved at lower temperature (Table 1) or in the solid state[15] and becomes adequate to efficiently bind oxygen from air.

The selective oxygen-binding to the CoP-PAP complex was volumetrically measured in the solid state (powder) (Figure 1).

Table 1. Oxygen-binding affinity (p_{50}) of the CoP complexes in DMF solution at 25 °C

Ligand	p_{50}/cmHg
PAP	70
PAP (5°C)	45
PAP (solid powder)	9.4
Pyridine	28
3,4-Diaminopyridine	38
Aniline	200

[CoP] = 0.1 mM, [Ligand]/[CoP] = 100, cmHg = 1333.22 Pa.

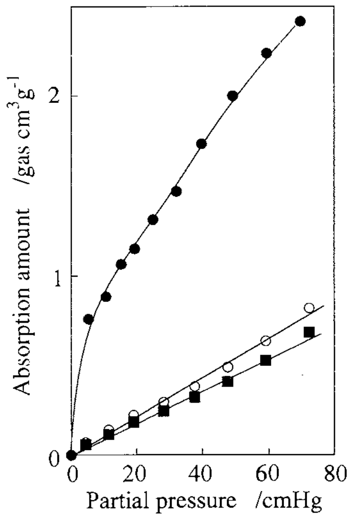


Figure 1. Absorption isotherms of oxygen and nitrogen for the powder of the CoP-PAP complex at 30°C: oxygen (●), nitrogen (■), oxygen for PAP (○). The absorption amounts were measured based on the pressure decrease of pure oxygen or nitrogen under the condition of constant volume.

The CoP-PAP complex (CoP = 17 wt%) absorbed 2.3 cm^3 oxygen/g polymer, which corresponded to 72 mol% of the fed CoP. The oxygen absorption amount was several times larger than those of physically dissolved oxygen and nitrogen. Figure 1 also indicates that the oxygen absorption follows a dual absorption based on a linear combination of Henry's law for the physical and Langmuir isotherm for the chemical absorption. The oxygen-binding affinity determined by the contribution of the Langmuir isotherm was p_{50} = 8.8 cmHg which agreed with that determined spectroscopically (Table 1). The CoP-PAP complex acted as an efficient oxygen absorbent.

The CoP-PAP complexes displayed electroconductivity of 5.8 $\times 10^{-6}$ S cm^{-1}.[16] The electroconductive and oxygen-carrying CoP-PAP complex will display a new performance based on its functions.

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11 Polymerization conditions: 3,4-Diaminopyridine 10 mM, CuCl 1.0 mM, pyridine 0.2 M, in DMF under oxygen at 25 °C for 24 h. Yield 58%.
12 The primary amino group of PAP was diazotized and coupled with 2-naphthol and to be converted to the azo derivatives, which was analyzed with its visible absorption (λ_{max} = 553 nm, $\varepsilon = 3.4 \times 10^3$ M^{-1}cm^{-1}).
13 The ESR signal gave an eight-line hyperfine splitting spectrum with the following parameters: $g_{\parallel}$ = 2.03, $g_{\perp}$= 2.29, and A^{Co} = 79 G. These agreed with the parameters previously repeated for the same CoP complexed with pyridine: F. A. Walker, *J. Am. Chem. Soc.*, **92**, 4235 (1970).
14 H. C. Brown and D. H. McDaniel, *J. Am. Chem. Soc.*, **77**, 3752 (1955).
15 This enhanced affinity in the solid state could be reduced by taking the oxygen solubility in DMF into account.
16 The electroconductivity of PAP was measured by using the four-probe method.