Electrocatalytic Four-Electron Reduction of Dioxygen by 1,2-Phenylene-Bridged Dicobalt Diporphyrins

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1,2-Phenylene-bridged dicobalt diporphyrin **1** catalyzes efficiently the four-electron reduction of dioxygen to water in acidic solution. The catalytic activity of the diporphyrin is strongly affected by the substituents on the phenyl rings attached to the porphyrin macrocycles.

The search for efficient catalysts for the four-electron reduction of dioxygen to water has been of great interest since such catalysts can be used in the oxygen cathodes of fuel cells.[1] However, there are thus far only a few molecular catalysts which can catalyze dioxygen reduction to water without producing significant amounts of hydrogen peroxide in acidic media.[2-5] One of the successful quests for such catalysts was to utilize cofacial diporphyrins in which two metal centers are in close proximity so that they can act jointly in binding and activating dioxygen molecules.[2,3] It has been known that the catalytic activities of the cofacial diporphyrins are sensitive to their structures. One of the structural factors controlling the catalytic activities is the number of atoms in the linkage(s) between the two porphyrins which is in turn related to the metal-metal distances in the cofacial diporphyrins.[2] Cofacial diporphyrins tested for the catalytic dioxygen reduction thus far have three or more atoms in the linkage(s).[2,3] Therefore, it would be interesting to see how well cofacial diporphyrins linked with *two-atom-bridge(s)* perform as catalysts for dioxygen reduction. Two of us recently reported the synthesis of such cofacial diporphyrins, 1,2-phenylene-bridged diporphyrins.[6] Here we report the electrocatalytic activities toward dioxygen reduction of three different 1,2-phenylene-bridged dicobalt diporphyrins **1**, **2** and **3** which differ in the substituents on the phenyl rings attached to the porphyrin macrocycles (Figure 1). Remarkably, *the dicobalt diporphyrin 1 catalyzes efficiently the four-electron reduction of dioxygen to water in acidic solution* without producing a significant amount of hydrogen peropxide.

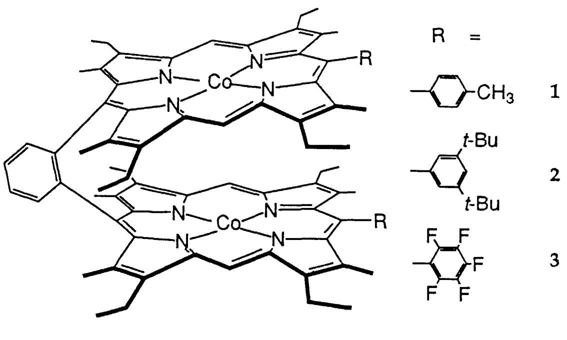

Figure 1. 1,2-Phenylene-bridged diporphyrins used in this study.

The cyclic voltammogram of **1** adsorbed on a graphite electrode in a deaerated acidic aqueous solution shows a quasi-reversible surface-confined redox couple whose potential (0.35 V vs NHE) is independent of pH up pH = 7. The catalytic reduction of dioxygen by this system is demonstrated by cyclic voltammetry and rotating ring-disk voltammetry[2,7] carried out in the oxygen

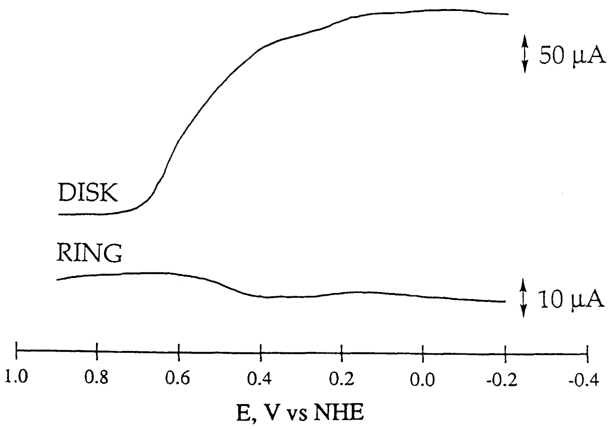

Figure 2. Rotating ring-disk voltammogram obtained with graphite disk electrode (area = 0.20 cm^2) coated with **1** and platinum ring electrode (H_2O_2 collection efficiency = 0.17) in oxygen saturated 0.1 M trifluoroacetic acid. Rotation rate = 100 rpm; scan rate of disk voltage = 5 mV sec^{-1}.

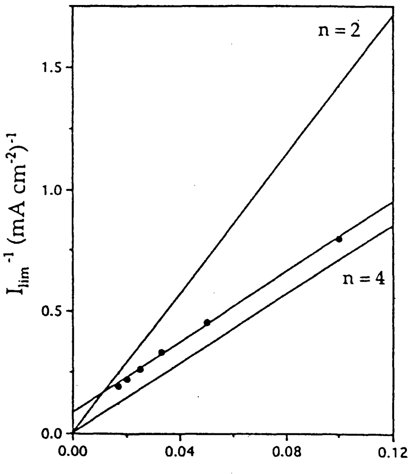

Figure 3. Koutecky-Levich plot for the reduction of O_2 at a rotating graphite disk electrode coated with **1** in oxygen saturated 0.1 M trifluoroacetic acid; n = 2 and n = 4 lines are the calculated responses for the two-electron and four-electron reduction of dioxygen, respectively.

saturated solution. Figure 2 displays a typical rotating ring-disk voltammogram obtained with **1** adsorbed on the graphite disk electrode in 0.1 M trifluoroacetic acid. Only a small amount of hydrogen peroxide are detected at the ring electrode as the cathodic disk current starts to flow and finally reaches a plateau. This indicates that the majority of dioxygen (>85%) is reduced to water in this system. The Koutecky-Levich plot[8] of (limiting current)$^{-1}$ vs. (rotation rate)$^{-1/2}$ (Figure 3) confirms that the four-electron pathway is the major pathway for the dioxygen reduction: the number of electrons consumed in this process determined from the slope of the plot is 3.8. The catalytic activity of **1** is almost comparable to those of the best known four-electron catalysts Co_2FTF4[2, 9] or Co_2DPB[3, 9] in terms of four-electron selectivity; however, the half-wave potential ($E_{1/2}$) for the former is somewhat less positive than those for the latter (Table 1).

We also examined the catalytic activities of **2** and **3**. Both rotating ring-disk voltammetry and Koutecky-Levich analysis revealed that **2** on graphite catalyzes almost exclusively the two-electron reduction pathway of dioxygen to hydrogen peroxide while **3** catalyzes both the two-electron and four-electron pathways in a ratio of 0.65 : 0.35 (Table 1). Monomeric cobalt porphyrin-like behavior of **2** in dioxygen reduction is presumably due to the steric bulkiness of *tert*-butyl groups on the phenyl rings which prevents the two porphyrin macrocycles from approaching each other to have a suitable geometry for the joint action in dioxygen reduction. On the other hand, both steric and electronic effect might be responsible for the dominance of the two-electron pathway over four-electron pathway catalyzed by **3**.

Table 1. Electrochemical data for the reduction of dioxygen catalyzed by 1,2-phenylene-bridged dicobalt diporphyrins and other dicobalt cofacial diporphyrins adsorbed on graphite electrodes

porphyrin	E_f[a]	$E_{1/2}$[b]	I_{lim}[c]	n[d]	electrolyte	ref
1	0.34	0.56	1.3	3.8	0.1 M TFA	*e*
	0.34	0.65	1.3	3.8	0.5 M TFA	*e*
2	*f*	0.44	0.7	1.9	0.1 M TFA	*e*
3	*f*	0.42	0.9	2.7	0.1 M TFA	*e*
Co(OEP)[g]	0.84	0.30	0.7	1.9	0.1 M TFA	*e*
Co_2FTF4	0.62/0.27	0.72	1.3	3.9	0.5 M TFA	2
Co_2DPB	0.64/0.34	0.70	*h*	3.7/8	0.5 M TFA	3

[a]Formal potential(V vs NHE) of the adsorbed porphyrin evaluated from the cyclic voltammetric peak potentials under N_2. [b]Half-wave potential (V vs NHE) for O_2 reduction at a rotating disk electrode (rotation rate = 100 rpm). [c]Limiting current density for the reduction of O_2 at 100 rpm (mA cm^{-2}). [d]Number of electrons consumed (determined from the slope of a Koutecky-Levich plot). [e]This work. [g]OEP = octaethylporphyrin. [h]Not reported.

In summary, we have shown that the novel 1,2-phenylene-bridged dicobalt diporphyrin **1** catalyzes efficiently the four-electron reduction of dioxygen to water in acidic solution. The catalytic activity of the diporphyrin is strongly affected by the substituents on the phenyl rings attached to the porphyrin macrocycles. This is the first example demonstrating that cofacial diporphyrins linked with a two-atom-bridge can catalyze the four-electron reduction of dioxygen. This work also suggests that the relative orientation of the two porphyrins may be as important as the metal-metal distance in achieving the four-electron reduction of dioxygen by cofacial diporphyrins. This work is being expanded to include other 1,2-phenylene-bridged diporphyrins bearing different substituents.

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References and Notes

1 D. J. Schiffrin, *Electrochemistry*, **8**, 126 (1983); B. Yeager, *Electrochim. Acta*, **29**, 1527 (1984); J. A. R. van Veen and J. F. van Vaar, *Rev. Inorg. Chem.*, **4**, 293 (1982); A. J. Appleby and F. R. Foulkes, *Fuel Cell Handbook*, Van Nostrand Reinhold, New York, 1989.

2 J. P. Collman, P. Denisevich, M. Marocco, C. Koval and F. C. Anson, *J. Am. Chem. Soc.*, **102**, 6027 (1080); R. R. Durand, C. S. Bencosme, J. P. Collman and F. C. Anson, *J. Am. Chem. Soc.*, **105**, 2710 (1983); H. Y. Liu, M. J. Weaver, C. B. Wang and C. K. Chang, *J. Electroanal. Chem. Interfacial Electrochem.*, **145**, 439 (1983).

3 C. K. Chang, H. Y. Liu, and I. Abdalmuhdi, *J. Am. Chem. Soc.*, **106**, 2725 (1984).

4 J. P. Collman and K. Kim, *J. Am. Chem. Soc.*, **108**, 7847 (1986).

5 C. Shi and F. C. Anson, *J. Am. Chem. Soc.*, **113**, 9564 (1991); C. Shi and F. C. Anson, *Inorg. Chem.*, **31**, 5078 (1982).

6 A. Osuka, S. Nakajima, T. Nagata, K. Maruyama and K. Toriumi, *Angew. Chem. Int. Ed. Engl.*, **30**, 582 (1991).

7 A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980.

8 J. Koutecky and V. G. Levich, *Zh. Fiz. Khim.*, **32**, 1565 (1958).

9 FTF4 = face-to-face 4: DPB = 1, 8-biphenylene diporphyrin. For full names refer the original papers.