二硫桥键钴卟啉二聚体的合成与电催化氧还原性能

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摘要: 成功合成了二硫桥键相连的钴卟啉二聚体2Co。通过循环伏安电化学方法测试, 在无水二氯甲烷溶剂中, 钴卟啉二聚体展示了3个氧化和2个还原峰, 表明此钴卟啉二聚体可以稳定多重负/正电荷。详细研究了在酸性条件下的钴卟啉二聚体的电催化氧还原性能。钴卟啉二聚体的电催化氧还原显示了高稳定性和高活性, 测得转移电子数为3.5~3.6之间。钴卟啉二聚体的电催化氧还原性能说明通过二硫键对钴卟啉单体二聚化可以提高钴卟啉的电催化氧还原性能。

关键词: 钴卟啉; 二聚体; 氧气; 电催化还原
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Disulfide-Bridged Dimeric Cobalt Porphyrin: Synthesis and Electroreduction of Dioxygen

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Abstract: A disulfide-bridged dimeric cobalt porphyrin 2Co has been successfully synthesized. The cyclic voltammogram (CV) curves of 2Co exhibited three oxidation and two reduction potentials in CH₂Cl₂, indicating that the 2Co enable stabilizing multi-negative and positive charges. The ORR catalytic property of 2Co in acid media were investigated. The reduction of O₂ using the dimer 2Co as catalyst showed high stability and activity to give the higher the value of transferred electrons number (n) between 3.5 and 3.6 under dioxygen. The catalytic performance of 2Co indicates that dimerization of cobalt porphyrins have a slightly positive influence on the catalytic properties for oxygen reduction reactions (ORRs) in the acidic medium.

Keywords: cobalt porphyrin; dimer; O₂; electroreduction
0 Introduction

The efficient catalysts are very essential to study oxygen reduction reactions (ORRs) \(^1\). Among the explored catalysts for ORRs, cobalt porphyrin complexes are significant researched compounds in past decades\(^2\). It was revealed that the catalytic property and selectivity of cobalt porphyrin complexes for ORRs are highly depend upon the molecular structures of investigated cobalt porphyrin\(^2\).

More than decades ago, the ORR catalytic properties of face-to-face (FTF) dimeric cobalt porphyrins (Chart 1) have been studied well\(^3\). FTF cobalt porphyrins are composed of two porphyrin macrocycles linked by various bridges located at the meso or \(\beta\) positions of the porphyrins\(^3\). FTF cobalt porphyrins show two/four-electron electrocatalytic reduction of \(O_2\) to \(H_2O_2/H_2O\), which strongly relies on their molecular structures\(^3\). However, to date, the ORR catalytic properties of non-FTF dimeric cobalt porphyrins have been little-studied.

Recently, the zinc porphyrin which containing disulfide ligands was synthesized from metalloporphyrin containing four acetylthio groups as precursor with high yield (Chart 1)\(^4\). This work makes us realize that disulfide-bridged dimeric cobalt porphyrin could be obtained from cobalt porphyrins containing only one acetylthio group at the meso position. Under this context, non-FTF dimeric cobalt porphyrins are expected as new candidates to investigate the ORR catalytic properties.

1 Experimental

The materials and instrument can be found in Supporting information. The synthetic scheme of 2Co is shown in Scheme 1.

Synthesis of Por: 2,2’-(phenylmethylene)bis(1H-pyrole) (4.44 g, 20 mmol), S-(4-formylphenyl) ethanethioate (1.80 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) were added into 500 mL \(CH_2Cl_2\). Then 0.5 mL trifluoroacetic acid (TFA) was added under \(N_2\) at room temperature. After 3 h, chloranil (4.90 g, 20 mmol) was added to the mixture. The solution was stirred for extra
1 h. The organic solvent was removed. The crude solid
was purified by silica gel column chromatography
(CH3Cl/ethyl acetate) and recrystallization by CH3Cl/
methanol mixture to get pure Por in 5.4% yield (370
mg, 0.54 mmol). 1H NMR (300 MHz, in CDCl3): δ 8.85
(d, 8H, Ph), 8.24 (m, 8H, Ph), 7.78 (m, 11H, Ph), 2.61
(s, 3H, Me), −2.79 (s, 2H, NH). UV-Vis (CH3Cl, λ / nm (ε)): 418 (4.38×104 L·mol⁻¹·cm⁻¹), 515 (1.8×104 L·
mol⁻¹·cm⁻¹), 549 (7.6×103 L·mol⁻¹·cm⁻¹), 593 (4.4×103
L·mol⁻¹·cm⁻¹), 648 (3.8×103 L·mol⁻¹·cm⁻¹).

Synthesis of 1Co: Compound Por (30 mg, 0.044
mmol) and excess cobalt salt were dissolved in 30 mL
CH3Cl/methanol (5:1, V/V) and the mixture was stirred
overnight at 25 °C. After the ending of reaction, the
obtained solid was purified by silica gel column chroma-
tography to collect 1Co with 90% yield (29 mg,
0.039 mmol). ESI-MS: Calced. for C29H29CoN₅O₅S:
745.15 [M]+, Found: 745.42, 701.83. UV-Vis (CH3Cl,
λ / nm (ε)): 410 (2.97×10⁴ L·mol⁻¹·cm⁻¹), 529 (1.8×10⁴
L·mol⁻¹·cm⁻¹). IR (KBr, cm⁻¹): 1 711, 613 for ν(C=O).

Synthesis of 2Co: The reaction mixture of the
water solution (1 mL) of methyamine (mass fraction:
40%) and 15 mL THF solution of 1Co (15 mg, 0.020
mmol) was stirred for overnight. The obtained solid was
washed with methanol and n-hexane to give 2Co in
90% yield (13 mg, 0.009 mmol). ESI-MS: Calced. for
UV-Vis (CH3Cl, λ / nm (ε)): 430 (1.85×10⁴ L·mol⁻¹·
cm⁻¹), 545 (1.3×10⁴ L·mol⁻¹·cm⁻¹). IR (KBr, cm⁻¹): 590
for ν(C=O).

2 Results and discussion

The building block Por as precursor was synthe-
sized by acid-catalyzed condensation reaction[5]. The
treatment of dipyrromethane, benzaldehyde and S-(4-
formylphenyl) ethanethioate under acidic condensa-
tion conditions gave Por in 5.4% yield (Fig.S1, Supporting
information). The regular coordination reaction made
the cobalt porphyrin 1Co in 90% yield, and then 1Co
was reacted with MeNH₂ (40% in water) in tetrahydro-
furan (THF) solution at room temperature under N₂ for
overnight[4] to give the target product 2Co in 85% yield.

The porphyrin Por and cobalt complexes, 1Co
and 2Co, were characterized by NMR, electrospray ion-
ization-mass spectroscopy (ESI-MS), IR, electron para-
magnetic resonance spectra, UV-Vis spectroscopies
and density functional theory (DFT) calculations. The
ESI-MS spectra of 1Co and 2Co showed clear m/z sig-
nals of the whole molecular structure and their ionized
pieces (Fig.S2 and S3). The IR spectra of 1Co and 2Co
showed the disappearance of CO stretching vibrations
belonging to the acetyltliio group at 1 711 cm⁻¹ through
disulfide-bridge formed reaction (Fig.S4). The 1H NMR
spectra were not recorded for 1Co and 2Co complexes
due to the paramagnetic property of cobalt(II) ions. To
investigate magnetic properties of the cobalt complexes,
electron paramagnetic resonance (EPR) spectra of 1Co
and 2Co were examined in CH₂Cl₂ at 298 K (Fig.S5).
The EPR spectra of 1Co and 2Co show the behaviors of
unpaired electrons in Co(II) porphyrins similar with
previous porphyrin cobalt complexes[8]. The optimized
molecular structures of 1Co and 2Co were obtained by
DFT calculation at B3LYP/6-31G(d)/SDD level with
Gaussian 09 (Fig.1 and S6). Monomer complex 1Co
shows a highly planar molecular structure like regular
[18]porphyrin and TPPCo (Chart 1)[2,7]. The non-FTF
dimer 2Co shows the V-shaped molecular structure
with two connected cobalt porphyrin units as a result of
the properties and torsion angle of the porphyrin-S-S-
porphyrin bond, instead of the face-to-face configura-
tion of FTF cobalt porphyrins[3-8].

The optical properties of cobalt porphyrins were
examined by UV-Vis absorption spectrum. The optical

![Six aryl groups of meso-positions were replaced with hydrogen atoms to reduce computational costs; Hydrogen atoms are omitted for clarity](image-url)
absorption spectra of Por, 1Co and 2Co in dichloromethane (DCM) are displayed in Fig.2. All the spectra displayed very sharp and narrow Soret-like bands with high molar extinction coefficients and Q-like bands in the near-IR region, which are similar with the typical porphyrin-like absorption. The Soret-like band of complex 1Co was observed at 410 nm, and the low-intensity Q-like band of 1Co was at 529 nm (Fig.2). Interestingly, the Soret- and Q-like bands of dimeric complex 2Co were observed at 430 and 545 nm, respectively, which were red-shifted compared with those of monomeric complex 1Co.

![Absorption spectra of Por (black line), 1Co (red line) and 2Co (blue line) in DCM at room temperature](image1)

The electrochemical properties of 1Co and 2Co were examined by cyclic voltammogram (CV) in CH\textsubscript{2}Cl\textsubscript{2} at room temperature. 0.1 mol·L\textsuperscript{-1} tetra-n-butylammonium perchlorate (TBAP) was chosen as supporting electrolyte (Fig.3). The monomeric compound 1Co exhibited three reversible one electron oxidation potentials at 0.66, 0.95 and 1.14 V (vs SCE), and two ir-/reversible one electron reduction potentials at −0.83 and −1.33 V (vs SCE), respectively. Our previous work revealed that TPPCo exhibits three reversible one electron oxidation potentials at 0.70, 0.97 and 1.15 V (vs SCE), and two irreversible one electron reduction potentials at −0.87 and −1.38 V (vs SCE), respectively. Besides, the first reduction of TPPCo is irreversible in CH\textsubscript{2}Cl\textsubscript{2} because the generated Co(I) from first reduction can coordinate with CH\textsubscript{2}Cl\textsubscript{2} solvent to form \( \sigma \)-bond product as Co-CH\textsubscript{2}Cl\textsuperscript{2}. However, the first reversible reduction of 1Co indicate a ring-centered electron transfer which is significant different from TPPCo due to the SAc substituent group as electron withdrawing group probably. The first and second oxidation of dimeric porphyrin complex 2Co are irreversible and reversible waves with two electrons transferred, respectively. The third oxidation of 2Co at 1.24 and 1.34 V (vs SCE) can be assigned to two porphyrin ring. First step reduction of 2Co were separated and located at −0.86 and −0.92 V (vs SCE) with one electron transfer while the second reduction is reversible at −1.42 V (vs SCE) with two electrons transfer together. In conclusion, the reduction potential of 2Co is similar to 1Co while the oxidation potential of 2Co is positively shifted. These CV results also indicate that the 1Co and 2Co can capture/lost multi-negative and multi-positive charges.

![CV curves of 1Co and 2Co in DCM](image2)

The ORRs performance of the monomeric 1Co and dimeric 2Co were investigated in 1 mol·L\textsuperscript{-1} HClO\textsubscript{4} solution under conventional loading of the catalyst being 0.1 mg·cm\textsuperscript{-2}. The CV of 1Co and 2Co are illustrated in Fig.4. For the CV measurements, the catalysts were adsorbed on an edge-plane pyrolytic graphite (EPPG) disk electrode under argon and O\textsubscript{2} in 1 mol·L\textsuperscript{-1} HClO\textsubscript{4} solution. No reductions of 1Co and 2Co were observed under argon in 1 mol·L\textsuperscript{-1} HClO\textsubscript{4} solution, but irreversible reductions were observed at \( E_n = 0.42 \) V (vs RHE) for 1Co and at 0.50 V (vs RHE) for 2Co under O\textsubscript{2} atmosphere in the solution. The CV data indicated that catalytic ORR of cobalt complexes 1Co and 2Co have been observed in 1 mol·L\textsuperscript{-1} HClO\textsubscript{4} solution.
cobalt complexes 1Co and 2Co, the linear sweep voltammetric measurements of them were examined in the oxygen-saturated 1 mol·L⁻¹ HClO₄ media (Fig. 5a and 5c). The values of n of ORRs for 1Co and 2Co were determined from steady-state limiting currents on the plateau of current-voltage curves. The Koutecky-Levich (Supporting information) plot gave the slope of diagnostic to estimate the values of n under measurement condition (Fig. 5b and 5d)⁷. The cobalt complexes showed the values of n of ORR being 2.8~3.5 for 1Co and 3.5~3.6 for 2Co over a potential range of 0.2~0.4 V (vs RHE) in the oxygen-saturated 1 mol·L⁻¹ HClO₄ solution. The TPPCo shows the value of n being 2 in air-saturated 1 mol·L⁻¹ HClO₄ solution in previous work⁷. In our tests, the complexes 1Co and 2Co both show bigger values of n than TPPCo. The reason of inducing the bigger values of n are probably the SA as electron-withdrawing group of 1Co and dimerization of 2Co⁷.

Fig. 4 CV curves of 1Co and 2Co absorbed on an EPPG electrode under Ar (dash line) and O₂ (solid line) in 1 mol·L⁻¹ HClO₄

Fig. 5 Current-voltage curves (a, c) and Koutecky-Levich plots (b, d) of 1Co and 2Co in 1 mol·L⁻¹ HClO₄
It is clear that the ORR of cobalt porphyrin complexes involves multi-electron reactions. The processes of ORR are divided into two types. One type is two-step process (Eq. 1 and 2). The other is a four-electron process (Eq. 3) and water is product of this process in acid solution\textsuperscript{7,10}. Therefore, two cobalt porphyrin complexes \textbf{1Co} and \textbf{2Co} produced the mixture of H$_2$O$_2$ and H$_2$O as products in acid media during oxygen electroreduction reaction because the values of $n$ of \textbf{1Co} and \textbf{2Co} were 2.8~3.5 and 3.5~3.6, respectively, over 0.2~0.4 V (vs RHE) potential range.

2e$^-$ process: $\text{H}_2\text{O} + 2\text{e}^- + \text{O}_2 \rightarrow \text{HO}_2^- + \text{OH}^- \quad (1)$

$2\text{e}^- + \text{H}_2\text{O} + \text{HO}_2^- \rightarrow 3\text{OH}^- \quad (2)$

4e$^-$ process: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad (3)$

The rotating ring-disk electrode (RRDE) were also measured under O$_2$ in HClO$_4$ solution (Fig.6). We found that the ring current of \textbf{1Co} and \textbf{2Co} both increased in the range of the disk potentials companying with the increased disk current. The disk currents of \textbf{1Co} and \textbf{2Co} both increased from 0.6 V, and the current plateau was arrived at around 0.3 V (vs RHE) for complexes \textbf{1Co} and \textbf{2Co}.

The calculated peroxide yields of compounds \textbf{1Co} and \textbf{2Co} were generated based on Eq. 6 (Supporting information) under these experimental acid conditions (Fig.7). We found that the ORR catalytic properties of \textbf{2Co} in acid solution is clearly enhanced relative to the monomeric cobalt porphyrin \textbf{1Co}. The peroxide yields formed upon the electroreduction of dioxygen for \textbf{2Co} was almost hold 15%, resulting in a calculated average $n$ of 3.6. The peroxide yields of \textbf{1Co} was in a range of 31%~34%, resulting in a calculated average $n$ of 3.2, under the same experimental conditions. Besides, we note that the average $n$ numbers obtained from the RRDE tests are in good agreement with those derived from the Koutecky-Levich plots, corroborating that in comparison to \textbf{1Co}, ORR catalyzed by \textbf{2Co} undergoes a process closer to the 4$e^-$ participated pathway (Eq.3).

The ORR long-time stabilities of \textbf{1Co} and \textbf{2Co} were examined by the chronoamperometric $I$-$t$ test at 0.16 V (vs RHE) as a constant potential to estimate the
key parameter for potential applications of these two cobalt complexes (Fig.8). The linear sweep voltammetry (LSV) curves of 1Co and 2Co were also investigated before and after the I-t test for further comparison. After 300 min continuous testing, the ORR current density of 2Co just dropped around 10%, but that of 1Co dropped more than 20%. This result indicates that the stability of 2Co is slightly better than 1Co.

Although the attempts to obtaining single crystal of 2Co to investigate clearly molecular structure failed, the reason of superior ORR catalytic properties of 2Co to 1Co is provided considering all collected data and DFT calculation. The mainly reason is likely due to its oligomer nature with two porphyrins brought to closer proximity by the disulfide linker which was defined by the optimized structure of 2Co under theoretical calculation (Fig.1 and S6)[2-3]. Previous studies have also shown that the formation of oligomer from molecular complexes is beneficial for their ORR activities[2-3]. In addition, the disulfide linker in 2Co might further facilitate the through-bond charge transportation, which is essential for the electrocatalyst based on metal-organic complexes[11]. Therefore, despite of the less-than-four electrons transferred and the end product of H2O2 and H2O mixture during ORR, the dimeric complex 2Co still manifests as a good ORR catalyst in the acidic medium.

![Fig.8 ORR stabilities of 1Co and 2Co examined by LSV curves (a, b) which taken before and after 300 min chronoamperometric I-t test (c, d)](image)

3 Conclusions

In summary, a disulfide-bridged non-FTF dimeric cobalt porphyrin 2Co has been synthesized from monomer cobalt porphyrin 1Co. The optimized structure of 2Co shows a non-FTF molecular configuration obtained by DFT calculation. The dimerization of porphyrin in 2Co produced a red-shifted UV-Vis absorption compared with the spectrum of 1Co. The CV measurements of 1Co and 2Co indicate that they both can stabilize multi-negative and positive charges. The catalytic activities for ORRs of 1Co and 2Co were investi-
gated in acid media. The values of $n$ during ORRs of 1Co and 2Co obtained from the RRDE tests and the Koutecky-Levich plots all indicate that the dimerization of cobalt porphyrins have a slightly positive influence on the catalytic properties for ORRs in the acidic medium. Further studies on the linear oligomers of other metal porphyrin complex to examine catalytic properties and to evaluate the relationship between catalytic properties and molecular structures for ORRs are currently underway in our lab.

Supporting information is available at http://www.wjhxxb.cn

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