

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 Dioxide

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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 dioxide. 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

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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 β 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.

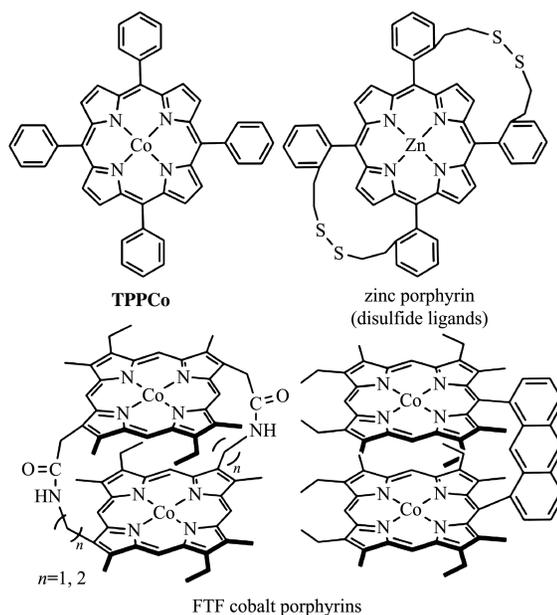
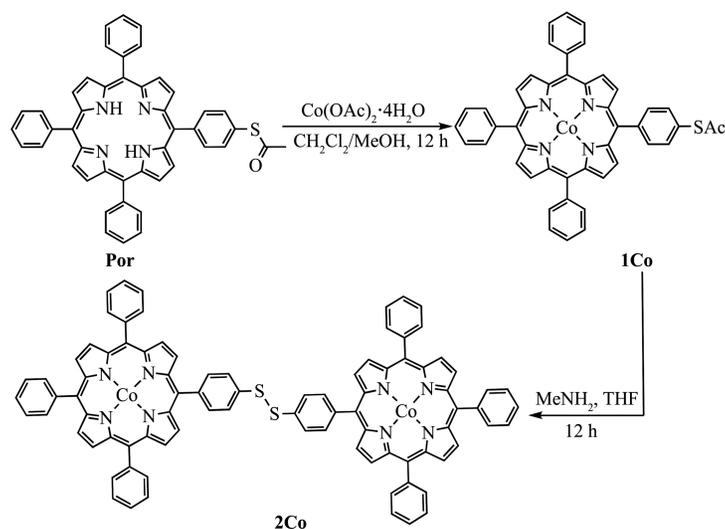


Chart 1 TPPCo, FTF cobalt porphyrins and zinc porphyrin containing disulfide ligands

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(1*H*-pyrrole) (4.44 g, 20 mmol), *S*-(4-formylphenyl) ethane-thioate (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



Scheme 1 Synthesis scheme of dimeric cobalt porphyrin **2Co**

1 h. The organic solvent was removed. The crude solid was purified by silica gel column chromatography (CH_2Cl_2 /ethyl acetate) and recrystallization by CH_2Cl_2 /methanol mixture to get pure **Por** in 5.4% yield (370 mg, 0.54 mmol). ^1H NMR (300 MHz, in CDCl_3): 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 (CH_2Cl_2 , λ / nm (ϵ)): 418 ($4.38 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 515 ($1.8 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 549 ($7.6 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 593 ($4.4 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 648 ($3.8 \times 10^3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$).

Synthesis of **1Co**: Compound **Por** (30 mg, 0.044 mmol) and excess cobalt salt were dissolved in 30 mL CH_2Cl_2 /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 chromatography to collect **1Co** with 90% yield (29 mg, 0.039 mmol). ESI-MS: Calcd. for $\text{C}_{46}\text{H}_{30}\text{CoN}_4\text{OS}$: 745.15 $[\text{M}]^+$, Found: 745.42, 701.83. UV-Vis (CH_2Cl_2 , λ / nm (ϵ)): 410 ($2.97 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 529 ($1.8 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). IR (KBr, cm^{-1}): 1 711, 613 for $\nu_{\text{C}=\text{O}}$.

Synthesis of **2Co**: The reaction mixture of the water solution (1 mL) of methylamine (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: Calcd. for $\text{C}_{88}\text{H}_{54}\text{Co}_2\text{N}_8\text{S}_2$: 1 404.26 $[\text{M}]^+$, Found: 1 404.42, 701.83. UV-Vis (CH_2Cl_2 , λ / nm (ϵ)): 430 ($1.85 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 545 ($1.3 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). IR (KBr, cm^{-1}): 590 for $\nu_{\text{S}=\text{S}}$.

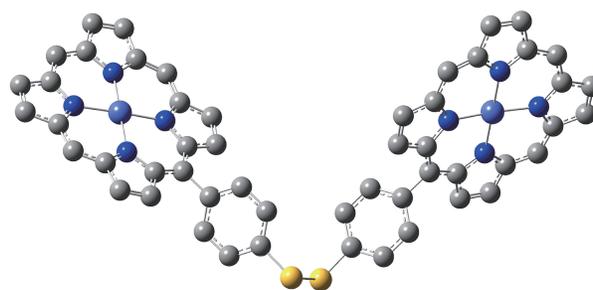
2 Results and discussion

The building block **Por** as precursor was synthesized by acid-catalyzed condensation reaction^[5]. The treatment of dipyrromethane, benzaldehyde and *S*-(4-formylphenyl) ethanethioate under acidic condensation 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 MeNH_2 (40% in water) in tetrahydrofuran (THF) solution at room temperature under N_2 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 ionization-mass spectroscopy (ESI-MS), IR, electron paramagnetic resonance spectra, UV-Vis spectroscopies and density functional theory (DFT) calculations. The ESI-MS spectra of **1Co** and **2Co** showed clear m/z signals 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 acetylthio 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 CH_2Cl_2 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^[6]. 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 configuration of FTF cobalt porphyrins^[3-4].

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

Fig.1 Optimized structure of **2Co** calculated at B3LYP/6-31G(d)/SDD level of DFT

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^[7]. 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**.

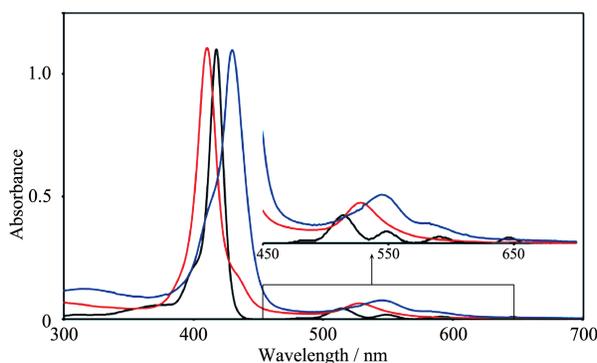
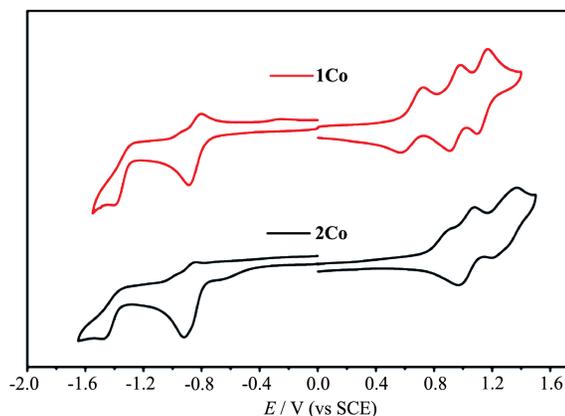


Fig.2 Absorption spectra of **Por** (black line), **1Co** (red line) and **2Co** (blue line) in DCM at room temperature

The electrochemical properties of **1Co** and **2Co** were examined by cyclic voltammogram (CV) in CH_2Cl_2 at room temperature. $0.1 \text{ mol} \cdot \text{L}^{-1}$ 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^[7]. 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^[7b]. Besides, the first reduction of **TPPCo** is irreversible in CH_2Cl_2 because the generated Co(I) from first reduction can coordinate with CH_2Cl_2 solvent to form σ -bond product as $\text{Co}-\text{CH}_2\text{Cl}$ ^[7]. 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^[7a]. 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^[7]. 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^[8].



Supporting electrolyte: $0.1 \text{ mol} \cdot \text{L}^{-1}$ TBAP, scan rate: $0.1 \text{ V} \cdot \text{s}^{-1}$

Fig.3 CV curves of **1Co** and **2Co** in DCM

The ORRs performance of the monomeric **1Co** and dimeric **2Co** were investigated in $1 \text{ mol} \cdot \text{L}^{-1}$ HClO_4 solution under conventional loading of the catalyst being $0.1 \text{ mg} \cdot \text{cm}^{-2}$ ^[7a,9]. 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_2 in $1 \text{ mol} \cdot \text{L}^{-1}$ HClO_4 solution. No reductions of **1Co** and **2Co** were observed under argon in $1 \text{ mol} \cdot \text{L}^{-1}$ HClO_4 solution, but irreversible reductions were observed at $E_{\text{pc}} = 0.42$ V (vs RHE) for **1Co** and at 0.50 V (vs RHE) for **2Co** under O_2 atmosphere in the solution. The CV data indicated that catalytic ORR of cobalt complexes **1Co** and **2Co** have been observed in $1 \text{ mol} \cdot \text{L}^{-1}$ HClO_4 solution.

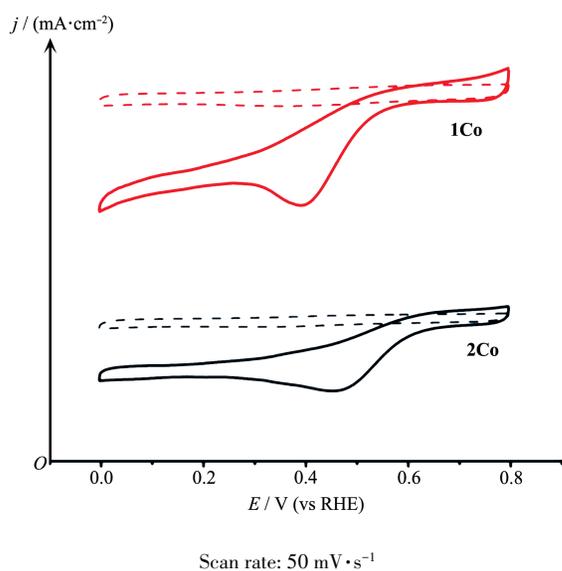


Fig.4 CV curves of **1Co** and **2Co** adsorbed on an EPPG electrode under Ar (dash line) and O₂ (solid line) in 1 mol·L⁻¹ HClO₄

To gain the values of transferred electrons number (n) during the electroreduction reaction of investigated

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 work^[7]. 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 SAC as electron-withdrawing group of **1Co** and dimerization of **2Co**^[7].

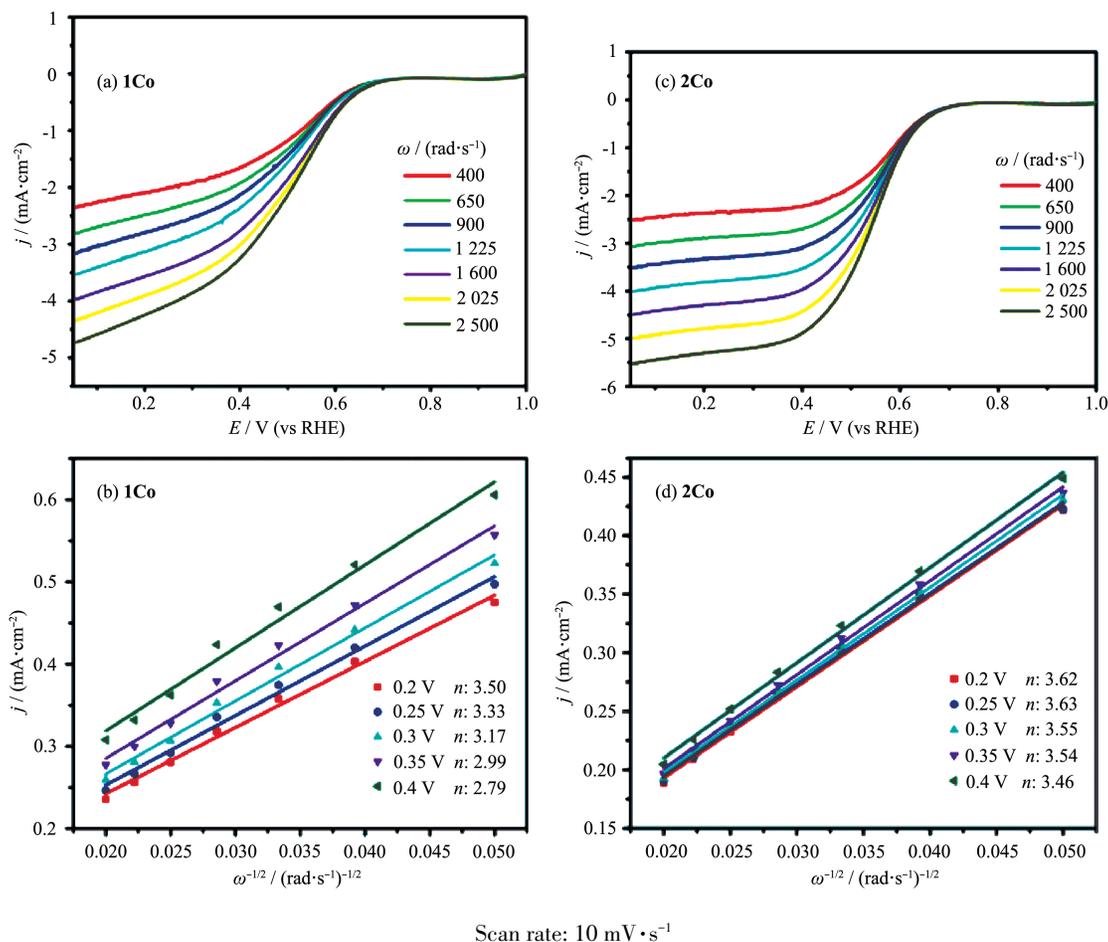
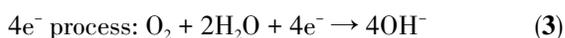
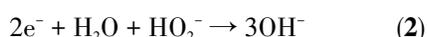
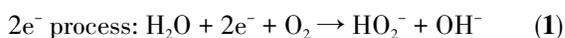


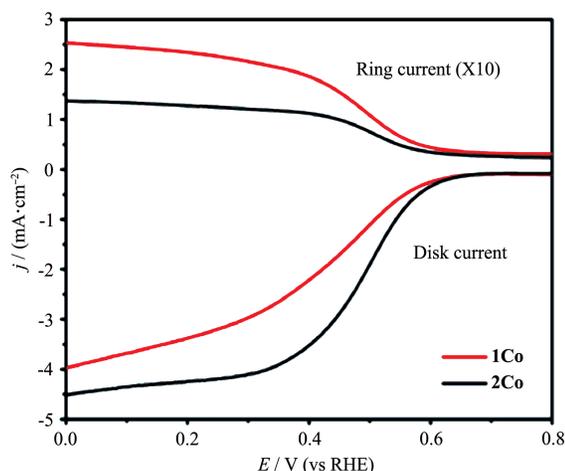
Fig.5 Current-voltage curves (a, c) and Koutecky-Levich plots (b, d) of **1Co** and **2Co** in 1 mol·L⁻¹ HClO₄

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^[7,10]. Therefore, two cobalt porphyrin complexes **1Co** and **2Co** produced the mixture of H₂O₂ and H₂O as products in acid media during oxygen electroreduction reaction because the values of *n* of **1Co** and **2Co** were 2.8~3.5 and 3.5~3.6, respectively, over 0.2~0.4 V (vs RHE) potential range.



The rotating ring-disk electrode (RRDE) were also measured under O₂ in HClO₄ solution (Fig.6). We found that the ring current of **1Co** and **2Co** both increased in the range of the disk potentials accompanying with the increased disk current. The disk currents of **1Co** and **2Co** both increased from 0.6 V, and the current plateau was arrived at around 0.3 V (vs RHE) for complexes **1Co** and **2Co**.

The calculated peroxide yields of compounds **1Co** and **2Co** were generated based on Eq. 6 (Supporting information) under these experimental acid conditions (Fig.7). We found that the ORR catalytic properties of **2Co** in acid solution is clearly enhanced relative to the monomeric cobalt porphyrin **1Co**. The peroxide yields formed upon the electroreduction of dioxygen for **2Co**

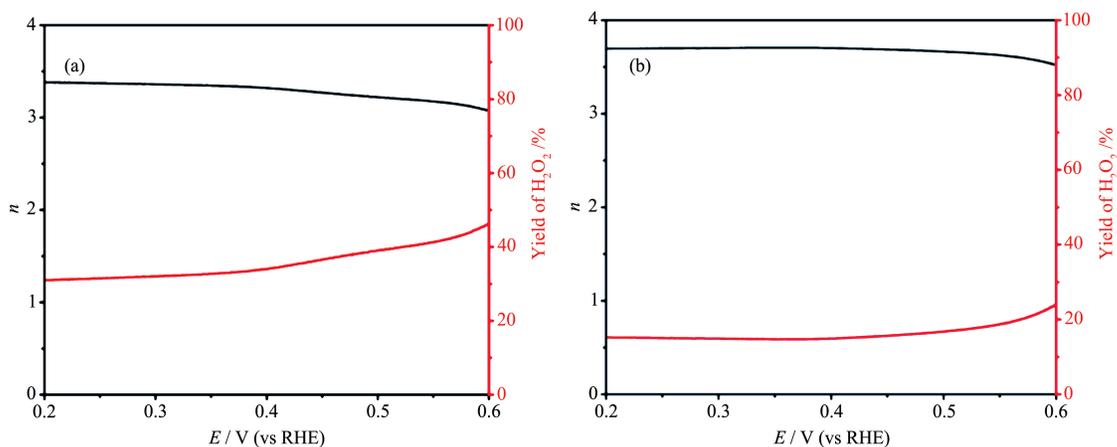


Potential of disk electrode was from 0.8 to 0 V (vs RHE);
Potential of ring electrode was held at 1.2 V (vs RHE);
Rotation rate was 1 600 r·min⁻¹, and the scan rate was 10 mV·s⁻¹

Fig.6 RRDE voltammograms of **1Co** and **2Co** under O₂ in HClO₄ solution

was almost hold 15%, resulting in a calculated average *n* of 3.6. The peroxide yields of **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 **1Co**, ORR catalyzed by **2Co** undergoes a process closer to the 4e⁻ participated pathway (Eq.3).

The ORR long-time stabilities of **1Co** and **2Co** were examined by the chronoamperometric *I-t* test at 0.16 V (vs RHE) as a constant potential to estimate the



Potential range was from 0.2 to 0.6 V (vs RHE)

Fig.7 Values of *n* and H₂O₂ yields of **1Co** (a) and **2Co** (b) under dioxygen in 1.0 mol·L⁻¹ HClO₄

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.

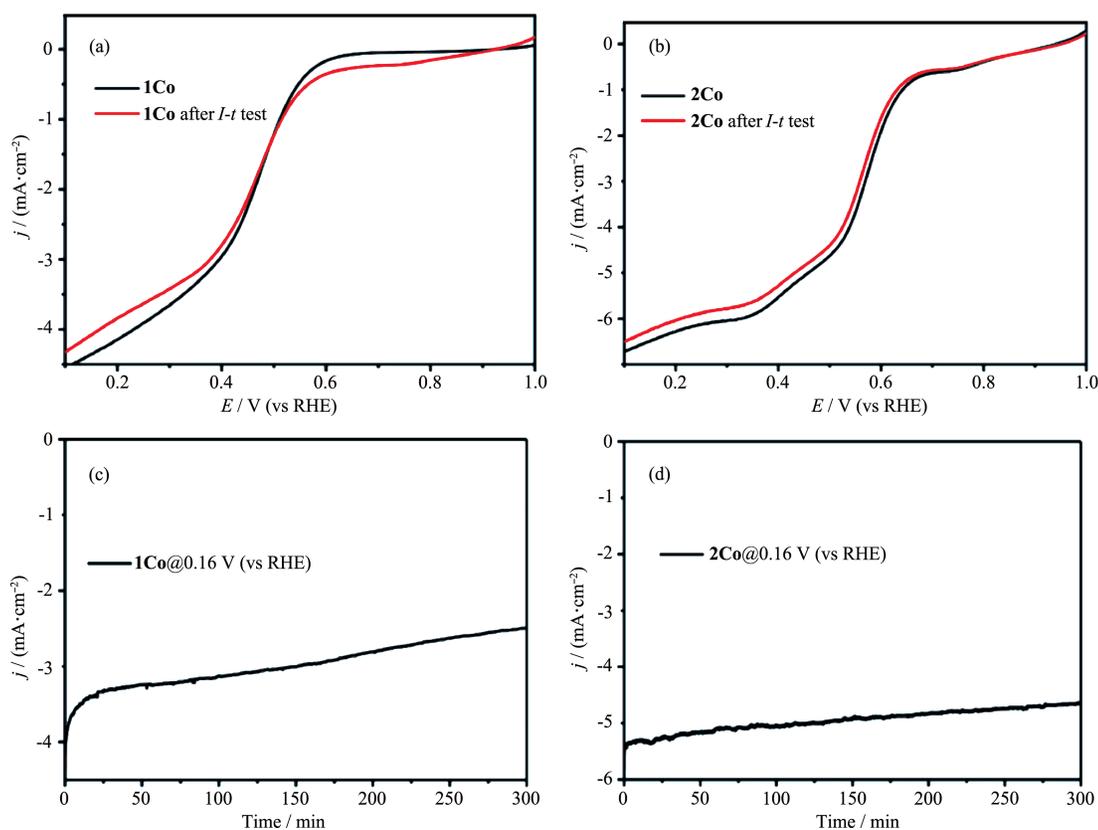


Fig.8 ORR stabilities of **1Co** and **2Co** examined by LSV curves (a, b) which taken before and after 300 min chronoamperometric *I-t* test (c, d)

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.wjhxzb.cn>

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