Triangular Trinuclear Metal-N$_4$ Complexes with High Electrocatalytic Activity for Oxygen Reduction

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S *Supporting Information*

ABSTRACT: A new class of macrocyclic metal-N$_4$ complexes $[MN_4]_n$ (M = Co and Fe) were designed and synthesized based on a triangular ligand. Their unique triangular trinuclear structure provides a high density of active sites and facilitates the reduction of dioxygen via a four-electron pathway. Among them, a $[CoN_4]_3$/C catalyst (20 wt %) exhibits high catalytic activity and long-time stability for the oxygen reduction reaction (ORR) in alkaline conditions, superior to the commercial Pt/C catalyst. Such structurally well-defined $[MN_4]_n$ complexes provide a platform for a new generation of nonprecious metal catalysts (NPMCs) for fuel cell applications.

Due to the potential energy crisis and the demand for environmental protection, fuel cells have attracted considerable interest in recent years as efficient and clean energy converters.[1,2] In present fuel cells, Pt nanoparticles supported on carbon black (Pt/C) remain the best cathode catalyst for the oxygen reduction reaction (ORR), which is the crucial reaction deciding the cell performance.[3,4] However, the high cost, the time dependent drift, and the carbon monoxide deactivation of the Pt-based catalysts are still big obstacles for the commercialization of fuel cells.[5] Searching for efficient, less expensive, and more abundant nonprecious metal catalysts (NPMCs) for ORRs therefore is an important issue from practical and theoretical points on fuel cell techniques.

Macrocyclic metal-N$_4$ complexes[6–12] as NPMCs have been developed for over five decades as a promising alternative to Pt catalysts for ORRs. And enormous efforts have been devoted to the study of various macrocyclic metal-N$_4$ complexes, including a single macrocycle,[6] cofacial macrocycle-based dimers,[8–12] and their derivatives with functional groups[13–15] that contain four nitrogen donors (i.e., metal-N$_4$ chelates). Up to now, however, very few complexes qualify as a catalyst for ORRs due to the low selectivity and poor stability.[10–12]

Herein, we present a new class of structurally well-defined macrocyclic metal-N$_4$ complexes as NPMCs for oxygen reduction. In particular, novel trinuclear metal-N$_4$ complexes $[MN_4]_n$ (M = Co (II) and Fe (II)) were synthesized from a novel triangular aromatic macrocycle as a ligand, in which three [16]-annulene like N$_4$-macrocycles were condensed in one conjugated plane via a central hexaazatrinaphthylene (Figure 1). The unique features including large planar conjugation and an unprecedented high density of active sites prompt the —O—O— cleavage and result
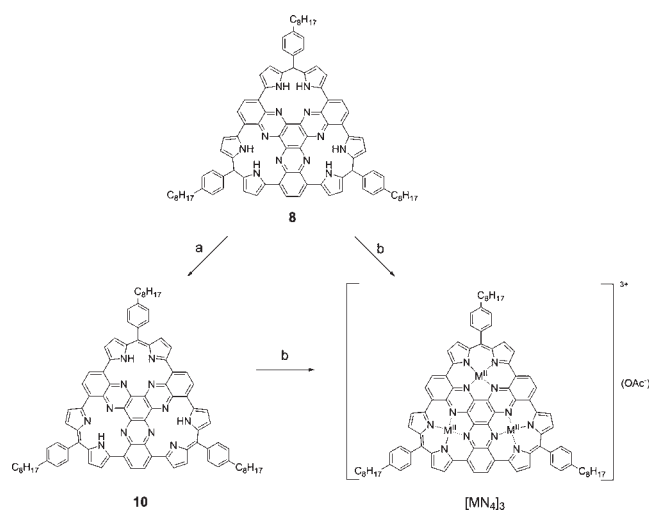

Figure 1. Synthesis of triangular trinuclear metal-N$_4$ complexes $[MN_4]_3$ (M = Co(II) and Fe(II)). The complexes $[MN_4]_3$ were prepared from **8** or **10**. Reaction conditions: (a) DDQ in DMF/Toluene, microwave: 2 h/140 °C/200 W; (b) Metal acetate in DMF, microwave: 4 h/190 °C/200 W.

in high catalytic activity and selectivity.[16] Indeed, $[CoN_4]_3$ with all three centers of the chelating ligand occupied by Co(II) ions was shown to catalyze an efficient four-electron ORR process with a much higher electrocatalytic activity and better long-term operation stability than those of the commercially available Pt/C catalyst in alkaline electrolytes. More important, our trinuclear metal-N$_4$ complexes $[MN_4]_n$ possess structurally defined catalytic sites for ORRs, which provides a platform for a new generation of NPMCs and presents an important advancement in the development of fuel cells.

The synthesis of the ligand 1,4,7,10,13,16-tris-[2′-(4″-octylphenyl-2H-pyrrole-2′-ylidenemetyhl)-1H-pyrrole-5′-yl]-5,6,11,12,17,18-hexaazatrinaphthylenes (**10**) started from the condensation of 2,3-diamino-1,4-dibromobenzene (**1**) with hexaketocyclohexane (**2**) to afford the hexabromohexaazatrinaphthalene core (**3**) (see Supporting Information).[17] Subsequent Suzuki coupling of **3** with 2-boronic acid of *N*-protected pyrrole (**4**) led to the protected hexapyrrolo-hexaazatrinaphthalene (**5**) in almost quantitative yield, which was thermally deprotected to

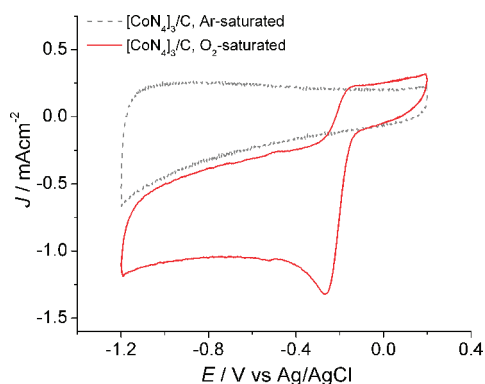**Figure 2.** Cyclic voltammograms of $[CoN_4]_3/C$ on a glassy-carbon RDE electrode at a scan rate of 100 mV/s in Ar-saturated and O_2-saturated aqueous solution of 0.1 M KOH. A catalyst loading of 25.45 μg/cm^2 was used for all RDE voltammograms.

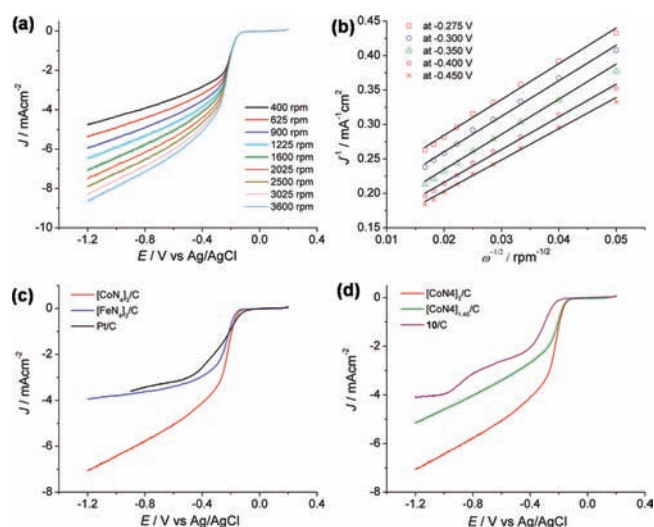**Figure 3.** (a) Rotating-disk electrode (RDE) linear sweep voltammograms of $[CoN_4]_3/C$ supported on a GC electrode in 0.1 M KOH saturated with O_2 at different rotation rates; (b) Koutechy-Levich plot of J^{-1} vs $w^{-1/2}$ at different electrode potentials. Symbols are experimental data obtained from (A), and lines are linear regressions. (c) ORR polarization curves for $[MN_4]_3/C$ catalysts (M = Co and Fe) and Pt/C (20 wt %) in 0.1 M KOH saturated with O_2; (d) ORR polarization curves for $[CoN_4]_3/C$, $[CoN_4]_{1.45}/C$, and 10/C. In (c) and (d), the electrode rotation rate is 1600 rpm and the scan rate is 10 mV/s. A catalyst loading of 25.45 μg/cm^2 was used for all RDE voltammograms, and the actual complex content in the catalyst was 20 wt %. Current densities were normalized in reference to the geometric area of the RDE (0.0707 cm^2).

produce hexapyrrolo-hexaazatrinaphthalene (**6**). 1,4,7,10,13,16-Tris-[2′,2″-(4‴-octylphenylmethylene)-bis-1H-pyrrole-5′,5″-yl]-5,-6,11,12,17,18-hexaazatrinaphthalene (**8**) was achieved via condensation of **6** with the p-n-octyl-benzaldehyde (**7**). And the dehydrogenation of **8** to the fully conjugated macrocycle **10** was then performed with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) (**9**) in toluene/DMF by microwave irradiation (Figure 1).

The metal complexation was executed via the acetate methods for porphyrins, where Co^{II}- and Fe^{II}-acetates were added in stoichiometric amounts to the DMF solution of **8** or **10** (Figure 1) (see Supporting Information).[18] Density functional theory (DFT) calculations of the ligand and of the metal complex indicate fully planar structures for both, with a Co—Co distance of 6.6 Å (Figure S4a,c,d). All $[MN_4]_n$ complexes tested in this report were supported on carbon black, denoted as $[MN_4]_n/C$ (20 wt % $[MN_4]_n$; see Supporting Information). Different from the adsorption on the surface of a pyrolytic graphite electrode,[6,9,14,15,19] utilization of a carbon black support will facilitate the future practical application in fuel cells.

Figure 2 shows the cyclic voltammogram (CV) curves of the $[CoN_4]_3/C$ in Ar-saturated (dotted curve) and O_2-saturated (solid curve) aqueous solution of 0.1 M KOH at a scan rate of 100 mV/s, respectively. As compared to no cathodic peak in the Ar-saturated solution, a significant enhancement of the cathodic peak at −0.26 V in the O_2-saturated solution indicates the electrocatalytic activity of $[CoN_4]_3/C$ for the ORR.

To gain further insight into the role of $[CoN_4]_3/C$ during the ORR electrochemical process, the reaction kinetics was studied by rotating disk voltammetry. Figure 3a presents the voltammetric profiles of $[CoN_4]_3/C$ in the O_2-saturated 0.1 M KOH electrolyte, where the current density enhances with increasing rotation rates (from 400 to 3600 rpm). The onset potential of $[CoN_4]_3/C$ for the ORR is approximately at −0.14 V, close to that (−0.13 V) obtained from CV measurements (Figure 2). Figure 3b depicts the corresponding Koutecky—Levich plots (vs) at various electrode potentials. The data exhibit good linearity, and the slopes remain approximately constant over the potential range from −0.275 to −0.450 V, suggesting similar electron transfer numbers for oxygen reduction at different electrode potentials. The linearity and parallelism of the plots are usually taken as an indication of first-order reaction kinetics with respect to the concentration of dissolved O_2.

We benchmarked the electrocatalytic properties of $[CoN_4]_3/C$ and $[FeN_4]_3/C$ against commercial Pt/C (20 wt % platinum

on Vulcan XC-72R). The same amount of catalysts by mass (25.45 μg/cm^2) was loaded onto a glass carbon (GC) rotating disk electrode (RDE). A characteristic set of polarization curves for the ORR on $[CoN_4]_3/C$, $[FeN_4]_3/C$, and Pt/C are displayed in Figure 3c. $[CoN_4]_3/C$ shows the same onset potential of −0.14 V as $[FeN_4]_3/C$, close to that of commercial Pt/C (−0.11 V). By using the Koutecky—Levich equations,[20,21] the number of electrons transferred (n) and kinetic limiting current density (J_K) were calculated and summarized in Table 1. Based on the analysis of the onset potential, n and J_K, for a given ligand **10**, Co(II) ions as the central metal ions in the $[MN_4]_n$ complexes exhibit better catalytic activities than Fe(II), which is different from the order of the MN_4 phthalocyanines.[22] Remarkably, the $[CoN_4]_3/C$ catalyst shows the highest selectivity and the highest mass activity of 9.63 mA/cm^2 at −0.35 V (Table 1), which is more than two times higher than that (4.44 mA/cm^2) of the commercial Pt/C catalyst (20 wt % platinum on Vulcan XC-72R) (Figure 3c). To the best of our knowledge, this is the first time such an excellent electrochemical performance in the ORR with transition metal N_4-chelate molecules has been observed.

As mentioned above, the nature of active sites for the ORR holds the key to the development of NPMCs. In comparison with the recently reported high performance NPMCs based on the mixture of the individual nitrogen-containing precursors and transition metal salts,[23,24] our structurally well-defined trinuclear complexes can provide more information about the relationship between molecular structure and the catalytic activity. Therefore, we further investigated the effect of different numbers of Co(II) ions on the catalytic activity for the ORR with metal-free ligand **10**, $[CoN_4]_{1.45}$, and $[CoN_4]_3$, as depicted in Figure 3d. First, $[CoN_4]_3/C$ and $[CoN_4]_{1.45}/C$ give the same onset potential

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Table 1. Summary of the Kinetic Parameters for Oxygen Reduction at $[CoN_4]_3$/C, $[CoN_4]_{1.45}$/C, 10/C, $[FeN_4]_3$/C, and the Reference Pt/C on GC Electrodes

	n^a	Onset potential $(V)^b$	J_K $(mA/cm^2)^c$	Durability
$[CoN_4]_3$/C	3.7	−0.14	9.63	84.0%
$[CoN_4]_{1.45}$/C	3.3	−0.14	7.00	73.5%
10/C	1.8	−0.20	3.00	73.5%
$[FeN_4]_3$/C	2.9	−0.15	4.80	27.2%
Pt/C	3.9	−0.11	4.44	52.5%

[a] The electrons transferred number (n) per O_2 molecule was calculated from eqs 1 and 2 in the Supporting Information. [b] The onset potentials were determined from rotating-disk voltammograms. [c] The kinetic current density at −0.35 V was derived from the Koutecky–Levich plots.
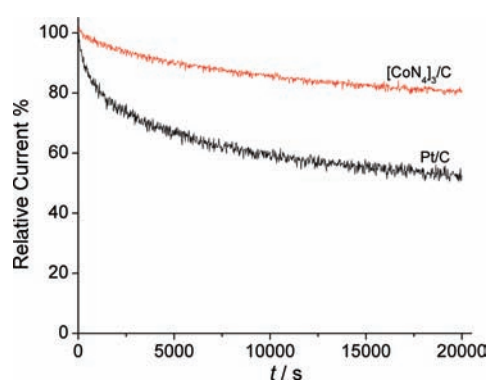

Figure 4. Current−time (i−t) chronoamperometric response of $[CoN_4]_3$/C and Pt/C modified GC electrode at −0.26 V in O_2-saturated aqueous solution of 0.1 M KOH at a rotation rate of 1600 rpm.

of −0.14 V, while **10**/C reveals a more negative potential of −0.20 V. Also, a significant decrease in the selectivity and activity ($n = 3.3$ and $J_K = 7.00$ mA/cm^2 for $[CoN_4]_{1.45}$/C and $n = 1.8$ and $J_K = 3.00$ mA/cm^2 for **10**/C respectively; Table 1) are derived when the number of the central Co ions changes from 1.45 to 0. Three points become obvious: (i) the ligand alone has catalytic activity for the ORR, which might be due to its nitrogen-containing conjugated framework, similar to the metal-free nitrogen-containing carbon materials;[20,25,26] (ii) the electrochemical activity of the $[CoN_4]_n$ complex is particularly sensitive to the first introduction of Co ions; and (iii) the higher metal content accounts for the increased catalytic activity in the $[CoN_4]_n$ complex.

Since durability is one of the major concerns in current fuel-cell technology, the stability of the $[CoN_4]_3$/C catalyst was further tested at a constant voltage of −0.26 V for 20000 s in an O_2-saturated aqueous solution of 0.1 M KOH at a rotation rate of 1600 rpm (Figure 4). Remarkably, the corresponding current−time (i−t) chronoamperometric response of $[CoN_4]_3$/C exhibits a very slow attenuation and a high relative current of 80.6% still persists after 20 000 s. In contrast, Pt/C shows a gradual decrease with a current loss of approximately 52.5% measured after 20 000 s. This result clearly suggests the durability of $[CoN_4]_3$/C is superior to that of the Pt/C catalyst.

In conclusion, we have designed and synthesized triangular trinuclear metal-N_4 complexes based on the construction of a planar conjugated macrocycle as a ligand. After coordination with three Co ions, the $[CoN_4]_3$ complex supported on carbon black as ORR catalysts reveals much better electrochemical activity and long-term stability than the commercially available Pt/C catalyst in alkaline electrolytes. Thus, our work leads to efficient, non-precious, and stable metal catalysts as alternatives of Pt in fuel cells and makes an important step toward a future "electromobility". Furthermore, the well-defined structures of these planar trinuclear metal-N_4 complexes provide more information about the nature of active sites, which will facilitate the design of a more magnificent structure with higher catalytic activity.

■ ASSOCIATED CONTENT

S **Supporting Information.** Synthesis of ligands and metal complexes, DFT calculations, structural characterizations, and electrochemical measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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