Electrocatalytic Reduction of Dioxygen by Diruthenium Cofacial Diporphyrins Axially-Bound to a Gold-Supported, Self-Assembled Monolayer

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A gold-supported, self-assembled monolayer containing imidazole termini provides axial binding sites for the diruthenium cofacial diporphyrins (μ-N_2)Ru_2(DPA)(CH_3CN) and (μ-N_2)-Ru_2(DPB)(CH_3CN). Cyclic voltammetry studies suggest that these electrode-bound molecules electrocatalytically reduce dioxygen.

The effort to understand the multielectron reduction of dioxygen has yielded many macrocyclic electrocatalysts that can reduce dioxygen,[1] but only a few achieve direct four-electron reduction to water.[2] Several metalated cofacial diporphyrins of the DPA and DPB family[3] can effect this four-electron reduction, but only when adsorbed on edge plane graphite electrodes (EPGE). EPGE is a complex, heterogeneous surface containing many functional groups (quinones, phenols, carboxylic acids, etc.) that are all potential axial ligands for the metal centers of the adsorbed porphyrins.[4] As early as 1979, oxygenated functionalities on the surface of the EPGE were thought to interact with the axial position of metalloporphyrins, thereby significantly influencing dioxygen reduction catalysis.[5] Recently, it was suggested that axial ligation from EPGE to the metal center for a series of iridium porphyrins is essential to triggering the direct four-electron catalytic reduction.[6] Specific characterization of the axial ligation promises a better understanding of the electrode's impact on the catalysis. The electrode's role can be clarified by binding catalysts via controlled axial ligation to an electrode that is more defined than EPGE.

This communication describes a novel method for attaching metalloporphyrin dioxygen reduction catalysts to a well-defined electrode surface as well as the demonstration of two new catalysts employing our attachment method. We believe this method of attachment can be exploited to characterize fully the catalyst−electrode interactions, including those which trigger the four-electron reduction catalysis of dioxygen by certain metalloporphyrins. Compared with the adsorption on EPGE, our method for attaching a catalyst to an electrode surface has the crucial advantage that the catalyst, even in its active state, can be observed spectroscopically.[7]

Gold-supported, self-assembled monolayers (SAMs) formed from *n*-alkyl mercaptans[8] can separate an electrode from a redox-active species via a thin, electrode-passivating hydrocarbon layer while still allowing the passage of current.[9] In the approach presented here, a mixed SAM was constructed with imidazoles protruding from a structured hydrocarbon sea. When this SAM was placed in a dilute solution of a diruthenium cofacial diporphyrin possessing weakly-bound acetonitrile axial ligands, a surface reaction occurred in which an acetonitrile ligand was displaced by an imidazole presented by the SAM.

The diruthenium cofacial diporphyrins, (μ-N_2)Ru_2(DPA)-(CH_3CN)$_2$ and (μ-N_2)Ru_2(DPB)(CH_3CN)$_2$, each have a labile dinitrogen bridged between two redox-active ruthenium centers, shown in Figure 1. The labile dinitrogen provides a pocket which is vulnerable to dioxygen substitution. These cofacial diporphyrins were chosen for this study because they closely resemble the monomeric porphyrins that have a well-understood chemistry with the mixed SAMs employed.[7]

(μ-N_2)Ru_2(DPB)(CH_3CN)$_2$ was synthesized from the metal−metal-bonded species Ru_2(DPB)[10] via the addition of acetonitrile under a dinitrogen atmosphere.[11] The greater distance between the metal centers in the DPA complex compared with the DPB complex precluded the use of a metal−metal-bonded intermediate to produce (μ-N_2)Ru_2(DPA)(CH_3CN)$_2$. Instead, the DPA complex was synthesized via the photolysis of the CO complex.[12]

The SAMs used in this study were formed by immersing a freshly prepared gold surface[13] in a dioxygen-free solution of 0.5 mM *n*-decyl mercaptan and 0.5 mM 1-(10-mercaptodecyl)-imidazole[14] for 48 h. The SAMs were removed from the absorbate solution, thoroughly rinsed, dried under a nitrogen stream, and characterized by optical ellipsometry, contact-angle goniometry, X-ray photoelectron spectroscopy (XPS), grazing-angle FT-IR, transmission UV−vis, STM, and electrochemistry.[7] The thickness of the resulting SAMs averaged 15 Å as determined by ellipsometry. Approximately one-fifth of all adsorbates contained an imidazole as determined by XPS N(1s) and C(1s) photoelectron peak intensities.

The diruthenium cofacial diporphyrins were deposited onto these SAMs, under an inert (N_2) atmosphere, from a stirred solution of 1 mM metalloporphyrin in dichloromethane. After 4 h, the surfaces were removed from the diporphyrin solution and thoroughly rinsed with dichloromethane and benzene. Once the surfaces had dried, they were again characterized[15] and subsequently employed in the electrochemical experiments. A schematic representation of the cofacial diporphyrin (μ-N_2)Ru_2-DPA(CH_3CN) bound to the SAM is presented in Figure 2.

We believe that O_2 replaces N_2 in the cavity between the two cofacial porphyrins in both the DPA and DPB systems when

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[12] Collman, J. P.; Ennis, M. S. Unpublished results. See Supporting Information for details.

[13] Gold (111) surfaces were prepared by electron-beam vapor deposition of either 10 nm of titanium followed by 100 nm of gold on polished, cleaned silicon (100) wafers (Pure-Sil) or 1 nm of titanium followed by 10 nm of gold on cleaned, plain glass slides (for UV−vis).

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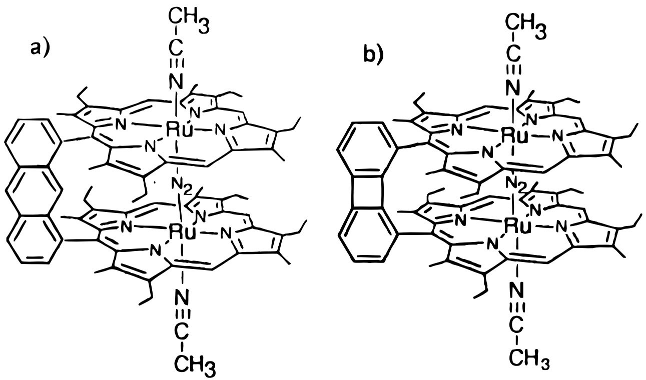

$(\mu\text{-N}_2)\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2$ $(\mu\text{-N}_2)\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})_2$

Figure 1. Line drawing representations of the cofacial diporphyrins used in these studies: (a) $(\mu\text{-N}_2)\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2$; (b) $(\mu\text{-N}_2)\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})_2$.

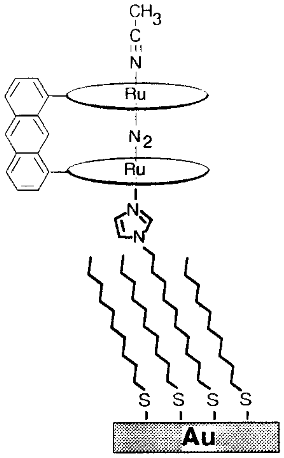

Figure 2. Schematic representation of $\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ attached to the mixed SAM. Ovals are used to represent the porphyrin rings.

exposed to dioxygen. The UV−vis spectra reveal the SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ Soret band shifts 2 nm from 402 to 404 nm when exposed to dioxygen. A corresponding SAM/$\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ Soret band shift was not observed.[16] Upon exposure of SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ to CO, an absorbance corresponding to a CO bound to ruthenium appeared in the IR spectrum (ν_{CO} 1955 cm^{-1}), consistent with the lability of the $\mu\text{-N}_2$.[17]

The electrochemical measurements of the SAMs were performed in a cell compromsed of a bored-out cone of poly(tetrafluoroethylene) pressed against the sample; the bore defines the electrode area (0.70 cm^2).[18] The electrolyte (0.1 M aqueous trifluoroacetic acid), counter electrode (gold wire), reference electrode (SCE), and needle were then placed in the bore which was covered with a plastic sheet. The electrolyte was saturated with a continuous flow of O_2. The resulting CVs for the SAMs with bound cofacial diporphyrins under an argon and subsequentially a dioxygen atmosphere are shown in Figure 3.

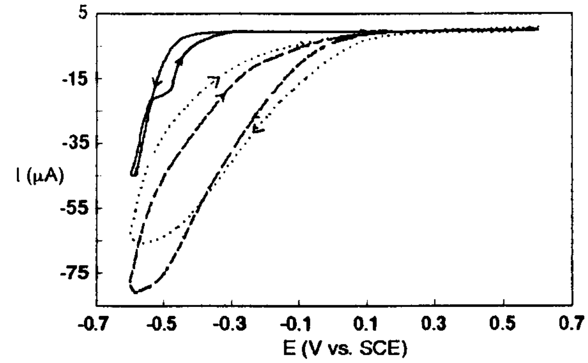

Figure 3. CVs of a mixed SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ under an argon atmosphere (solid line), a mixed SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ (dashed line), and a mixed SAM/$\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ (dotted line) in O_2-saturated 0.1 M trifluoroacetic acid. Scan rate = 20 mV/s.

Evidence for electrocatalytic activity was the appearance of dioxygen reduction waves when the SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ and SAM/$\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ precatalysts were placed under a continuous flow of dioxygen. The catalytic dioxygen reduction waves are several orders of magnitude larger than the surface metalloporphyrin redox waves for the same systems under an inert atmosphere at a scan rate of 20 mV/s. In both systems, these dioxygen reduction waves disappeared with argon purging but reappeared when the electrolyte was once again saturated with dioxygen. Very little difference between the electrocatalytic activities of the two cofacial diporphyrins was observed, which suggests that the difference in bridge length does not significantly affect the rate of activity. The CV for the catalyst-free SAM showed no evidence of electrocatalysis whether the electrolyte was purged with dioxygen or argon, indicating that SAM-bound cofacial diporphyrins are the active catalysts. These SAM-bound diruthenium cofacial diporphyrins are unprecedented examples of dioxygen reduction catalysts employing two ruthenium centers. A monomeric $\text{Ru}(\text{TMP})(\text{N}_2)$[19] bound to an identical SAM showed no catalytic activity under the same reaction conditions.

Further work is under way both to determine whether these diruthenium cofacial diporphyrins effect the four-electron reduction of dioxygen to water and to understand electrode−catalyst interactions more fully. Incorporating known functionality on highly-ordered SAMs, using the technique described here, should enhance our overall understanding of dioxygen reduction catalyzed by metalloporphyrins.

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Supporting Information Available: Text giving synthetic details and characterization of $(\mu\text{-N}_2)\text{Ru}_2(\text{DPB})(\text{CH}_3\text{CN})_2$ and $(\mu\text{-N}_2)\text{Ru}_2(\text{DPA})(\text{CH}_3\text{CN})_2$ (2 pages). Ordering information is given on any current masthead page.

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(15) The SAM/$\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ thickness averaged 26 Å, and the SAM/$\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})(\mu\text{-N}_2)$ thickness averaged 25 Å using a refractive index of 1.50. The same surface characterization techniques that were used on the SAM without diporphyrin were used on these surfaces. These data and comparisons with monomeric porphyrin deposition results strongly imply that the diruthenium cofacial diporphyrins on the surface are fairly represented by Figure 2.

(16) The measured Soret shift is at our detection limit; the Q-bands were not seen in the UV−vis spectra of the diporphyrin attached SAMs.

(17) Lyophilized powders of $(\mu\text{-N}_2)\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2$ and $(\mu\text{-N}_2)\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})_2$ placed under an NH_3 atmosphere undergo selective replacement of the dinitrogens to give $\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2(\text{NH}_3)_2$ and $\text{Ru}_2\text{DPB}(\text{CH}_3\text{CN})_2(\text{NH}_3)_2$, respectively. In solution (toluene), pyrazine also selectively replaces the dinitrogen of both the DPA and DPB complexes to give the corresponding acetonitrile complexes with a bridging pyrazine, $(\mu\text{-pyrazine})\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2$ and $(\mu\text{-pyrazine})\text{Ru}_2\text{DPA}(\text{CH}_3\text{CN})_2$. Collman, J. P.; Ennis, M. S. Unpublished Results.

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(19) TMP = *meso*-tetramesitylporphyrin. Substitution chemistry for the SAM/$\text{Ru}(\text{TMP})(\text{N}_2)$ is described in: Collman, J. P.; Ennis, M. S.; Offord, D. A; Griffin, J. H. *J. Am. Chem. Soc.*, manuscript in preparation.