Unusual Stability of a Bacteriochlorin Electrocatalyst under Reductive Conditions. A Case Study on CO2 Conversion to CO


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ABSTRACT: Photosynthetic CO2 fixation is mediated by the enzyme RuBisCo, which employs a nonredox-active metal (Mg2+) to bind CO2 adjacent to an organic ligand that provides reducing equivalents for CO2 fixation. Attempts to use porphyrins as ligands in reductive catalysis have typically encountered severe stability issues owing to ligand reduction. Here, a synthetic zinc–bacteriochlorin is reported as an effective and robust electrocatalyst for CO2 reduction to CO with an overpotential of 330 mV, without undergoing porphyrin-like ligand degradation (or demetalation) even after prolonged bulk electrolysis. The reaction has a CO Faradaic efficiency of 92% and sustains a total current density of 2.3 mA/cm2 at −1.9 V vs Ag/AgCl. DFT calculations highlight the molecular origin of the observed stability and provide insights into catalytic steps. This bioinspired study opens avenues for the application of bacteriochlorin compounds for reductive electrocatalysis with extended life beyond that seen with porphyrin counterparts.

KEYWORDS: bacteriochlorin, CO2 conversion, electrocatalysis, hydrogenation, porphyrin

INTRODUCTION

The photosynthetic fixation of carbon, a global process of immense ecological importance, is catalyzed by the enzyme RuBisCo. While an elaborate protein architecture, the enzyme-mediated reduction relies on a nonredox-active metal (Mg2+) and an organic ligand that provides reducing equivalents. Efforts toward abiological carbon fixation typically have turned to use redox-active metals.1–6 Metalloporphyrins have been widely used as tetradeutate ligands in photo- and electrocatalysis7,8,11–10 and are particularly attractive in part given the availability of mature synthetic routes to access structurally sophisticated architectures.11–14 However, though some porphyrin systems are stable enough under mild electrochemical conditions,15 a long-standing problem of porphyrin ligands—regardless of the nature or presence of the metal—is their instability under reductive and protic conditions, forming chlorins (C,C′-dihydroporphyrins), phlorins (C,N-dihydroporphyrins), isobacteriachlorins (tetrahydroporphyrins), or a mixture thereof by hydrogenation of one or both of the double bonds in the porphyrin 2H-pyrole rings (Chart 1A).16–20 Such undesired transformation leads to low Faradaic efficiency of electrocatalysis because some of the reducing equivalents are supplied to drive the 2e−/2H+ or 4e−/4H+ hydrogenation reactions.19–21 In addition, the resulting chlorin and phlorin catalysts have different light-harvesting properties and charge-separated states when compared to their precursors,22,23 which complicates the photocatalytic processes.19,20,24–26 For example, our previous work with Sb–porphyrin complexes has shown efficient hydrogen evolution but also irreversible porphyrin ligand reduction and thus low Faradaic efficiency.27 In a series of rhenium–porphyrin dyads for CO2 photoreduction, Windle et al. found that photoabsorption by the porphyrin induced 2-electron hydrogenation to form a chlorin first followed by another 2-electron hydrogenation to form an isobacteriachlorin, ultimately completely altering the Q-band region of the porphyrin spectrum.27 Such instability currently hinders the greater practical utility of porphyrins in applications to reductive electrocatalysis.

Bacteriochlorins are the core chromophores of natural bacteriochlorophylls that are already reduced so they are not vulnerable to hydrogenation reactions of a 2H-pyrole ring as in porphyrins. In addition, synthetic bacteriochlorins28–30 that are equipped with a geminal dimethyl group in each reduced (pyrrole) unit have been shown to be stable toward adventitious dehydrogenation (Chart 1B). These bacterio-
chlorins exhibit superior stability versus porphyrins, and their absorption spectrum can be easily tuned throughout the UV, visible, and near-infrared (NIR) regions by suitable modifications with substituents along the Q\textsubscript{ax} axis.\textsuperscript{28} Bacteriochlorins have already been used as chromophores for light-harvesting,\textsuperscript{31–33} as photosensitizers for photodynamic therapy,\textsuperscript{34,35} and as fluorophores for clinical diagnostics and cell imaging,\textsuperscript{30,36} but up to now have not been explored as ligands in electrochemistry and catalysis.

Here, we report the synthesis and characterization of a gem-dimethyl-substituted zinc(II) bacteriochlorin. As proof-of-concept, the zinc–bacteriochlorin complex was found to be a stable and efficient electrocatalyst for CO\textsubscript{2}-to-CO conversion as shown by the rather high (92%) Faradaic efficiency. To the best of our knowledge, this is the first demonstration of a bacteriochlorin ligand for efficient electrocatalysis.

RESULTS AND DISCUSSION

The zinc–bacteriochlorin ZnBC (Chart 1C) was prepared by following a reported procedure\textsuperscript{37} and was characterized by ICP-MS (Table S1) to confirm the complete removal of free zinc or other possible metal salts (NaCl, etc.) that could otherwise interfere in the catalytic process. The electrochemical properties of ZnBC were studied by cyclic voltammetry (CV) using glassy carbon as the working electrode in DMF with 5 M water and 0.5 mM of ZnBC and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte.

Under reducing conditions, the cyclic voltammogram of ZnBC shows two reversible peaks at −0.95 and −1.37 V vs Ag/AgCl (Figure 1), corresponding to the radical anion and dianion, respectively. The plots of peak current versus square root of the scan rate are linear (Figure 1 inset), indicative of diffusion-controlled processes.

Reduction potentials calculated by density functional theory (DFT)\textsuperscript{38} are in broad agreement with the experimental results, yielding calculated potentials of −1.03 and −1.65 V vs Ag/AgCl. Notably, calculations show that the reducing equivalents are delocalized on the bacteriochlorin ring, with negligible changes of electron density on the metallic center. The resulting electron density has essentially the same distribution as in the LUMO of the parent species (Figure S1A). Therefore, the calculations suggest that ZnBC has a redox-active ligand and a redox-innocent metal center, akin to zinc porphyrin systems from our group.\textsuperscript{9} Redox noninnocence of ligands has attracted much attention in catalysis, and the resulting changes in electron distribution suggest mechanistic implications.\textsuperscript{39} Notably, the geometry of ZnBC changes very little upon reduction, showing just a slight puckering of the ring with an N–N–N–N dihedral angle increase from a nearly planar 1° in the nonreduced case to 3° and 4° in the singly and doubly reduced cases, respectively (Figure S1B).

Catalytic CO\textsubscript{2} electroreduction was first seen by comparing CV measurements under an argon or CO\textsubscript{2} atmosphere, using DMF containing water (5 M) as the proton source (Figure 2A). In an argon atmosphere, significant current was observed after −1.8 V vs Ag/AgCl, attributed to proton reduction at this highly negative potential (red trace in Figure 2A). In a CO\textsubscript{2} atmosphere, a cathodic current increase was observed at the less negative potential of −1.5 V vs Ag/AgCl (blue trace in Figure 2A), corresponding to CO\textsubscript{2} reduction with an overpotential of 330 mV (the corrected thermodynamic potential in DMF/H\textsubscript{2}O (5 M) is 1.17 V, see the Supporting Information for details).

Controlled-potential electrolysis (CPE) of ZnBC at various potentials was performed for electrochemical CO\textsubscript{2} reduction in
DMF with 5 M water, using high-surface-area carbon fiber paper as the working electrode. 1H NMR spectroscopy and gas chromatography allowed detection of liquid and gaseous products. At all selected potentials, no liquid product was detected (Figure S2). Only CO and H2 were detected as the gaseous products. The CO Faradaic efficiency and total current density at various potentials are shown in Figure 3A. With more negative potentials applied to the catalyst electrode, higher CO Faradaic efficiency and total current densities were observed. The highest CO Faradaic efficiency of 92% and total current density of 2.3 mA/cm² were achieved at −1.9 V vs Ag/AgCl. This potential (−1.9 V vs Ag/AgCl) was selected for CPE. High CO Faradaic efficiency (92%) and total current density (2.3 mA/cm²) were held for over 4 h (Figure 3B), indicating excellent stability of the catalyst ZnBC. CPE using zinc-free bacteriochlorin under the same electrocatalytic conditions did not afford any detectable CO₂ reduction product, suggesting the role of the zinc center as a binding site for CO₂.

To confirm that the molecular integrity of ZnBC is retained and that no bacteriochlorin ligand degradation or demetalation occurred during bulk electrolysis, the UV–vis–NIR spectra of the electrolyte solution were recorded before and after the bulk electrolysis (Figure 2B). The two spectra are nearly identical, indicating no ligand degradation or demetalation during CPE. Transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS) were also performed on the carbon fiber paper after CPE (Figure S3). The absence of the zinc signal in the EDS and XPS spectra ruled out the possibility of zinc demetalation at the carbon electrode. The carbon electrode was gently washed with DMF after a 4-h electrolysis and again used as the working electrode in a fresh electrolyte solution without ZnBC. No CO₂ reduction was observed, further confirming that the active species for CO₂ reduction is ZnBC under homogeneous conditions rather than deposited ZnBC or zinc metal on the carbon electrode.

Potential binding modes of CO₂ on ZnBC were examined via DFT calculations (Figure 4). Comparing the minimum energy binding configurations of CO₂ on ZnBC in its nonreduced form as well as after the first and second reduction indicates that significant activation of the C–O bond occurs only after the second reduction. Without two reductions, CO₂ remains unreactive. However, upon the second reduction, CO₂ is reduced in agreement with the open circuit absorption spectrum and CV results. A full mechanistic analysis is outside the scope of this paper and will be reported elsewhere including additional experimental and computational results, consistent with CO₂ binding to the doubly reduced ZnBC complex.
To further probe the stability of the bacteriochlorin ligand, absorption spectroscopy was used to monitor the changes of free-base bacteriochlorin BC and porphyrin Porph (Chart 2).

Chart 2. Bacteriochlorin BC and Porphyrin Porph for Stability Comparison

The fluorinated porphyrin Porph was selected for comparison because of the following: (1) the first two reduction potentials of Porph are close (within 0.2 V difference) to those of BC, which helps minimize effects arising from the different redox properties of the bacteriochlorin and porphyrin; and (2) Porph has sufficient solubility in DMF with 5 M H2O, while many other porphyrins are poorly soluble (0.5 mM) in the same mixed solvent. During the stability test at −1.9 V vs Ag/AgCl, aliquots of the solution were taken out of the electrolysis cell and exposed to air for 5 min before absorption measurement. The shape and intensity of the absorption spectra of BC remained almost unchanged over the first 4 h. A 30% loss of spectral intensity was observed (albeit without a concurrent change in spectral shape) after an additional 20 h, indicating some degradation occurred during 20 h of electrolysis. In comparison, the absorption spectra of Porph underwent a dramatic change; the Soret band intensity decreased by 60% within the first 3 h, with a shape change and intensity increase in the Q-band region (Figure S4). The two new bands at 650 and 730 nm were attributed to the generation of two porphyrin hydrogenation products, phlorin and isobacteriochlorin. Prolonged electrolysis (a total of 22 h) led to complete bleaching of the porphyrin bands, even under strongly reducing conditions. Finally, we note that the present approach is bioinspired in two respects. First, the enzyme for photosynthetic carbon fixation, RuBisCo, relies on nonredox-active Mg(II) and an organic ligand that provides reducing equivalents. Second, the strategy of using gem-dialkyl groups to secure the stability of a tetrapyrrole macrocycle mirrors the natural electrocatalytic macrocycles, cobalamin and F430, which are pervasively substituted with gem-dialkyl groups in the reduced rings.

CONCLUSIONS

In conclusion, we have studied the electrochemical properties of a novel zinc(II)—bacteriochlorin complex under severe reducing conditions. A comparison between the bacteriochlorin ligand and a porphyrin analogue confirmed the superior stability of the bacteriochlorin. Application of the zinc–bacteriochlorin complex to electrocatalytic CO2-to-CO conversion resulted in high Faradaic efficiency (92%) and excellent catalyst stability. No ligand decomposition or zinc demetalation occurred during prolonged bulk electrolysis, indicating a truly molecular catalytic species. Computational results compared favorably with experimental voltammogram evidence suggesting that CO2 binding is induced upon double reduction of ZnBC. To the best of our knowledge, this is the first study of a bacteriochlorin ligand for efficient electro-catalysis. Our findings suggest the viability of employing bacteriochlorin-based catalysts for various catalytic processes, even under strongly reducing conditions. Finally, we note that the present approach is bioinspired in two respects. First, the enzyme for photosynthetic carbon fixation, RuBisCo, relies on nonredox-active Mg(II) and an organic ligand that provides reducing equivalents. Second, the strategy of using gem-dialkyl groups to secure the stability of a tetrapyrrole macrocycle mirrors the natural electrocatalytic macrocycles, cobalamin and F430, which are pervasively substituted with gem-dialkyl groups in the reduced rings.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.8b02991. Instruments, experimental details, additional figures, and additional computation and characterization data (PDF)

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Notes

The authors declare no competing financial interest.


