

ELECTROCATALYSIS

Reduced ring makes catalyst sing

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Chances are, if you have ever cut your finger (or mixed pyrrole with an aldehyde), you have handled a porphyrin. Such tetrapyrrolic macrocycles can exist in partially saturated forms and are found in abundance in nature, such as in chlorophyll, cofactor F₄₃₀, vitamin B₁₂, tunichlorin and porphyrinogens. Indeed, saturated porphyrins appear to be of great importance; for example, cofactor F₄₃₀ constitutes 7% of the microbial mats that are found in CH₄ seeps in the Black Sea. Partially saturated species such as F₄₃₀ and tunichlorin, in which one of the pyrrole groups is hydrogenated, are known as chlorins — catalytic motifs that are exploited for reduction reactions such as methanogenesis. As for the choice of metal, several chlorins — including tunichlorin, a complex isolated by Kenneth Rinehart and colleagues in 1988 — have been obtained as their Ni derivatives.

Ni porphyrins are active catalysts for the evolution of H₂ from H₂O, an electroreduction of great interest in the energy sector. Writing in *Chemical Science*, a team led by Jun-Long Zhang

disclose the catalytic performance of Ni chlorins, which are the partially hydrogenated cousins of the more well-studied Ni porphyrins. Inspired by Rinehart's work, Zhang hypothesized that tunichlorin is an algal pigment and thus could have potential use in H₂ evolution. To unravel the catalytic utility of tunichlorin, his team prepared a series of Ni model complexes and evaluated their potential as H₂ evolution catalysts. First, they prepared a pentafluorophenyl-substituted porphyrin and then used Woollin's reagent to selectively hydrogenate one pyrrole group to yield the chlorin. Last, they inserted Ni into both the porphyrin and the chlorin, and compared the two complexes. With respect to their redox properties, the two-electron reduction of the Ni chlorin occurred at a less negative potential than that of the Ni porphyrin. Both complexes are electrocatalysts for H₂ evolution, operating at Faradaic efficiencies in excess of 90%. However, the turnover frequency of the chlorin is 24 times greater than that of the porphyrin.

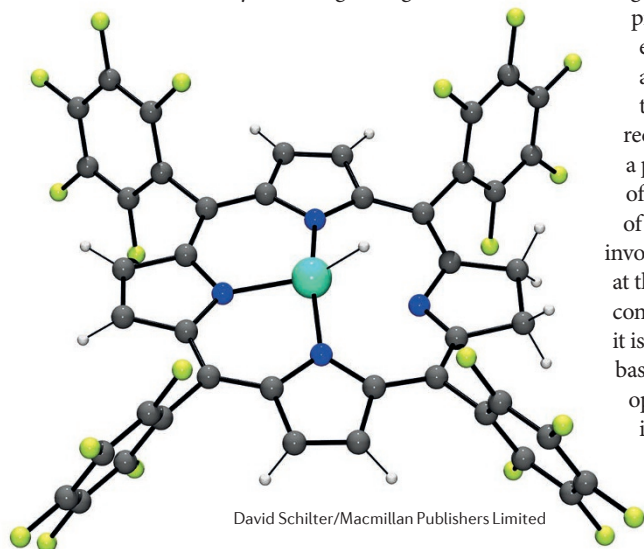
The results were rationalized using theoretical calculations, which predicted that injection of two electrons into the Ni porphyrin affords a Ni(II) complex of a tetranionic macrocycle, whereas reduction of the Ni chlorin gives a product with Ni(I) in the centre of a trianionic ligand. In the case of the Ni porphyrin, catalysis involves protonation of the dianion at the N atom of one pyrrole. By contrast, in the Ni chlorin dianion, it is the metal centre that is more basic, such that the catalyst operates through a Ni hydride intermediate. The barrier to the respective intermediates is 3.3 kcal mol⁻¹ lower for the Ni chlorin, and

protonation of the Ni hydride to give H₂ is exothermic by 31.9 kcal mol⁻¹. To corroborate this experimentally, Zhang and co-workers treated the Ni complexes of the porphyrin and chlorin with decamethylcobaltocene to generate the reactive dianions. Monitoring the UV–vis signatures upon treatment with acid showed that the Ni chlorin reacts an order of magnitude faster.

It was found that minor alterations to a ligand affected the electronic structure of the system to such a degree that a catalyst could be diverted into a distinct mechanism with vastly different reaction rates. “β-Hydrogenation interrupts delocalization on the ligand such that, after two-electron reduction of the complexes, more electron density resides on Ni in the chlorin derivatives, which thus prefer to operate via a nickel hydride,” explains Zhang. In terms of advancing the field, Zhang notes that this work tests our fundamental understanding of natural metal cofactors and provides an opportunity to design better molecular catalysts. So how will the team follow this up? “The next step is to investigate the role that the hydroxyl group in tunichlorin plays in hydrogen evolution,” mentions Zhang. “But we have a long way to go on H₂ evolution in the aqueous phase as well as CO₂ reduction.” Zhang's investigation helps us to further shine light onto Mother Nature's secrets and reminds us that if nature spends resources doing something, it is probably for a good reason.

Christopher Windle, Associate Editor,
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