De Novo Designed Artificial Cu Proteins (ArCuPs) as O-H/O-O/C-H Activation Catalysts

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ABSTRACT

Petroleum and natural gas are abundant feedstocks that provide the building blocks for producing fuels and fine-chemicals. Therefore, selective activation of C-H bonds of hydrocarbons in these feedstocks by chemical or biological means under environmentally benign conditions is highly sought-after - yet a challenging endeavour. Cu-containing metalloenzymes are excellent catalysts for functionalization of a wide range of C-H bonds employing molecular oxygen/H_2O_2 as a terminal oxidant. I will describe our approaches to develop a new generation of de novo designed, water-soluble artificial Cu proteins (ArCuPs) as sustainable biomolecular catalysts demonstrating peroxidase, oxidase, and C-H oxidation activity. Specifically, this approach produces well-characterized and stable metallopeptide catalysts that can activate C-H bonds of abiotic substrates both homogenously and electrochemically. A reductive priming to access the Cu-oxygen species is deemed beneficial for the reactivity and mechanistic outcome. Fine-tuning of the outer coordination sphere interactions further enhances the k_{cat}/K_m by up to ~80%. Functional relevance of our results with respect to biological C-H activation will be discussed.

KEY WORDS

De novo metalloenzymes; Copper proteins; C-H activation; Peroxygenation; Electrocatalysis

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