Artificial metalloenzyme for enantioselective sulfoxidation based on vanadyl-loaded streptavidin

JournalArticle (Originalarbeit in einer wissenschaftlichen Zeitschrift)

ID 116755
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Year 2008
Title Artificial metalloenzyme for enantioselective sulfoxidation based on vanadyl-loaded streptavidin
Journal Journal of the American Chemical Society
Volume 130
Number 25
Pages / **Article-Number** 8085-8
Keywords Coordination sphere; Stereochemistry; Sulfoxidation (artificial metalloenzyme for enantioselective sulfoxidn. based on incorporation of vanadyl into biotin-binding pocket of streptavidin); Sulfides Role: BSU (Biological study, unclassified), BIOL (Biological study) (artificial metalloenzyme for enantioselective sulfoxidn. based on incorporation of vanadyl into biotin-binding pocket of streptavidin); Protein motifs (biotin-binding pocket; artificial metalloenzyme for enantioselective sulfoxidn. b
Nature's catalysts are specifically evolved to carry out efficient and selective reactions. Recent developments in biotechnology have allowed the rapid optimization of existing enzymes for enantioselective processes. However, the ex nihilo creation of catalytic activity from a noncatalytic protein scaffold remains very challenging. Herein, we describe the creation of an artificial enzyme upon incorporation of a vanadyl ion into the biotin-binding pocket of streptavidin, a protein devoid of catalytic activity. The resulting artificial metalloenzyme catalyzes the enantioselective oxidation of prochiral sulfides with good enantioselectivities both for dialkyl and alkyl-aryl substrates (up to 93% enantiomeric excess). Electron paragmagnetic resonance spectroscopy, chemical modification, and mutagenesis studies suggest that the vanadyl ion is located within the biotin-binding pocket and interacts only via second coordination sphere contacts with streptavidin.
Publisher American Chemical Society
ISSN/ISBN 0002-7863 ; 1520-5126
edoc-URL http://edoc.unibas.ch/dok/A5254471
Full Text on edoc No;
Digital Object Identifier DOI 10.1021/ja8017219
PubMed ID http://www.ncbi.nlm.nih.gov/pubmed/18507383
ISI-Number WOS:000256962000064
Document type (ISI) Journal Article