

Armed by Asp? C-terminal carboxylate in a Dap-branched peptide and consequences in the binding of Cu^{II} and electrocatalytic water oxidation.

Autorzy

Łukasz Szyrwił
Dávid Lukács
Dávid Srankó
Zsolt Kerner
Aleksandra Kotynia
Justyna Brasuń
Bartosz Setner
Zbigniew Szewczuk
Katarzyna Malec
József Sándor Pap

Rok wydania

2017

Czasopismo

RSC Advances

Numer woluminu

7

Strony

24657-24666

DOI

10.1039/c7ra03814c

Kolekcja

Naukowa

Język

Angielski

Streszczenie

The imidazole ring of histidine (His) and the methylcarboxylate function of aspartic acid (Asp) are crucial for Cu coordination in enzymes, artificial proteins and other bioinspired systems. In order to elucidate the effect of Asp at the C-terminus, a new branched peptide, H-Gly-Dap(H-Gly)-Asp-NH₂ (2GD, Dap ¼ 2,3-diaminopropionic acid) has been synthesized to ligate Cu^I. While at pH < 8, 2GD favours dimeric complexes at 1 : 1 metal-to-ligand ratio, at increasingly alkaline pH the Asp at the C-terminus creates a {NH₂,N,N,O}_{eq} set and the dominance of mononuclear CuLH₂ and CuLH₃ species, according to potentiometry, molecular spectroscopy (UV-visible, circular dichroism and X-band electron paramagnetic resonance) and ESI-MS analysis. The changes in speciation with pH are accompanied by shifts in the Cu^{III}/II redox current peaks that were analyzed by square wave voltammetry (SWV) and allowed the calculation of the pK_a values for the Cu^I and Cu^{III} forms. The 2GD complex exhibits electrocatalytic activity in water oxidation in phosphate buffer. However, when Asp residues are present at all three termini to produce 3D (H-Asp-Dap(H-Asp)-Asp-NH₂), the electrocatalysis of water oxidation decreases and, if present only at the N-termini in 2DG (H-Asp-Dap(H-Asp)-Gly-NH₂), it ceases. As for Cu^I ligated by 2GD, a TOF of 16 s⁻¹ was calculated at pH ¼ 11 in 0.2 M phosphate electrolyte, which is crucial for catalysis, but also acts as inhibitor anion according to cyclic voltammetry observations. The system is highly tolerant to the presence of chloride, which is a feature of practical importance in

Typ publikacji

Artykuł

Licencja otwartego dostępu

CC-BY

Licencja na prawach której można swobodnie kopiować, rozprowadzać, zmieniać i remiksować objęty prawem autorskim utwór (Utwór-przedmiot prawa autorskiego) pod warunkiem podania imienia i nazwiska autora utworu pierwotnego oraz źródła pochodzenia utworu.

Pełny tekst licencji:

<https://creativecommons.org/licenses/by/3.0/pl/legalcode>

Adres publiczny

<http://dx.doi.org/10.1039/c7ra03814c>

Strona internetowa wydawcy

<https://www.rsc.org/>

Plik został wygenerowany dnia 2026-08-19 12:53:26

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/2mxbixf>.