Stepwise effective molarities in porphyrin oligomer complexes : preorganization results in exceptionally strong chelate cooperativity.

Autorzy

H. J. Hogben

J. K. Sprafke

M. Hoffmann

Miłosz Pawlicki

Harry L. Anderson

Rok wydania

2011

Czasopismo

Journal of the American Chemical Society

Numer woluminu

133

Strony

20962-20969

DOI

10.1021/ja209254r

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Complexes of zinc porphyrin oligomers with multivalent ligands can be denatured by adding a large excess of a monodentate ligand, such as quinuclidine. We have used denaturation titrations to determine the stabilities of the complexes of a cyclic zinc–porphyrin hexamer with multidentate ligands with two to six pyridyl coordination sites. The corresponding complexes of linear porphyrin oligomers were also investigated. The results reveal that the stepwise effective molarities (EMs) for the third through sixth intramolecular coordination events with the cyclic hexamer are extremely high (EM = 10^2–10^3 M), whereas the values for the linear porphyrin oligomers are modest (EM ≈ 0.05 M). The speciation profiles for the denaturation reactions demonstrate that intermediate species are not significantly populated and that these equilibria are well described by a highly cooperative two-state model.

Adres publiczny

https://doi.org/10.1021/ja209254r

Strona internetowa wydawcy

https://www.acs.org/content/acs/en.html