Aggregation and metal-complexation behaviour of THPP porphyrin in ethanol/water solutions as function of pH

Marco Zannotti, Rita Giovannetti, Babak Minofar, David Řeha, Lydie Plačková, Chiara A. D'Amato, Elena Rommozzi, Hanna V. Dudko, Nuerguli Kari, Marco Minicucci

PII:	S1386-1425(17)30995-2
DOI:	doi:10.1016/j.saa.2017.12.021
Reference:	SAA 15666
To appear in:	*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*
Received date:	1 June 2017
Revised date:	29 November 2017
Accepted date:	4 December 2017

Please cite this article as: Marco Zannotti, Rita Giovannetti, Babak Minofar, David Řeha, Lydie Plačková, Chiara A. D'Amato, Elena Rommozzi, Hanna V. Dudko, Nuerguli Kari, Marco Minicucci , Aggregation and metal-complexation behaviour of THPP porphyrin in ethanol/water solutions as function of pH. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Saa(2017), doi:10.1016/j.saa.2017.12.021

Aggregation and metal-complexation behaviour of THPP porphyrin in ethanol/water solutions as function of pH

Marco Zannotti*[a], Rita Giovannetti*[a], Babak Minofar*[b], David Řeha[b,c], Lydie Plačková [b,c], Chiara A. D'Amato[a], Elena Rommozzi[a], Hanna V. Dudko[d], Nuerguli Kari[a,e], Marco Minicucci[f]

[a] Chemistry Division, School of Science and Technology, University of Camerino (MC), Via Sant'Agostino 1, 62032, Camerino, Italy

[b] Faculty of Science, University of South Bohemia, Branišovská 1760, 37005 České Budějovice, Czech Republic

[c] Center for Nanobiology and Structural Biology, Institute of Microbiology, Academy of Sciences of the Czech Republic, Zamek 136, Nové Hrady, Czech Republic

[d] Biological Faculty, Belarusian State University, 4 Independence Square, Minsk, 220030, Belarus

[e] College of Chemistry and Chemical Engineering, Xinjiang University, 666 Shengli Road, 830046, Urumqi, Xinjiang, PR China

[f] Physic Division, School of Science and Technology, University of Camerino (MC), Via Madonna delle Carceri, 62032, Camerino, Italy

*Corresponding authors

Email addresses:

marco.zannotti@unicam.it, rita.giovannetti@unicam.it, minofar@nh.cas.cz

Keywords: Porphyrin dyes; Aggregation; Binary solvent mixture; Spectroscopic characterization; Molecular Dynamics simulations

Abstract

The effect of pH change on 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (THPP) with its aggregation as function of water-ethanol mixture was studied with UV-vis, fluorescence, Raman and computational analysis. In neutral pH, THPP was present as free-base and, increasing the water amount, aggregation occurred with the formation of H- and J- aggregates. The aggregation constant and the concentration of dimers were calculated, other information about the dimer aggregation were evaluated by computational study.

In acidic pH, by the insertions of two hydrogens in the porphyrin rings, the porphyrin changed its geometry with a ring deformation confirmed by red-shifted spectrum and quenching in fluorescence; at this low pH, increasing the water amount, the acidic form $(THPPH_2)^{2+}$ resulted more stable due to a polar environment with stronger interaction by hydrogen bonding.

In basic pH, reached by NH_4OH, THPP porphyrin was able to react with alkali metals in order to form sitting-atop complex (M_2THPP) confirmed by the typical absorption spectrum of metallo-porphyrin, Raman spectroscopy and by computational analysis.