Accepted Manuscript

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PII: S1386-1425(17)30618-2
DOI: doi: 10.1016/j.saa.2017.07.059
Reference: SAA 15346

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received date: 21 March 2017
Revised date: 21 July 2017
Accepted date: 30 July 2017

Please cite this article as: P. Bhyrappa, M. Sankar , Effect of solvent on the electronic absorption spectral properties of some mixed β-octasubstituted Zn(II)-tetraphenylporphyrins, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2017), doi: 10.1016/j.saa.2017.07.059

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ABSTRACT

A series of mixed β-octasubstituted Zn(II)-porphyrins, 2,3,12,13-tetra(chloro/cyano/methyl)-5,7,8,10,15,17,18,20-octaphenylporphinato zinc(II), $ZnTPP(Ph)_4X_4$ (X = CN, Cl and CH_3) have been examined by electronic absorption spectroscopy in various solvents. These Zn(II)-porphyrins exhibited varying degree of red-shift of absorption bands as high as 20-30 nm in 'B' band and 50-60 nm in longest wavelength band, 'Q(0,0)' band in polar solvents relative to that found in nonpolar solvents. The red-shift of B and Q(0,0) bands showed an unusual trend, $ZnTPP(Ph)_4(CN)_4$ > $ZnTPP(Ph)_4(CH_3)_4$ > $ZnTPP(Ph)_4Cl_4$ but fails to follow an anticipated anodic shift in first porphyrin ring oxidation (Vs Ag/AgCl) potential: $ZnTPP(Ph)_4(CN)_4$ (1.02 V) > $ZnTPP(Ph)_4Cl_4$ (0.74 V) > $ZnTPP(Ph)_4(CH_3)_4$ (0.38 V). Such a trend suggests the combined effect of non-planarity of the macrocycle and electronic effect of the peripheral substituents. The equilibrium constants for the binding of nitrogenous bases with the Zn(II)-porphyrins showed as high as twenty fold increase for $ZnTPP(Ph)_4X_4$ (X = Br and CN) relative to $ZnTPP(Ph)_4(CH_3)_4$ and follow the order: $ZnTPP(Ph)_4(CN)_4$ > $ZnTPP(Ph)_4Br_4$ > $ZnTPP(Ph)_4(CH_3)_4$ ≤ ZnTPP which is approximately in line with an increase in anodic shift of their first ring redox potentials