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Effect of solvent on the electronic absorption spectral properties of some mixed β -octasubstituted Zn(II)-tetraphenylporphyrins

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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)₄X₄ (X = CN, Cl and CH₃) 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(CH₃)₄ > ZnTPP(Ph)₄Cl₄ 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)₄Cl₄ (0.74 V) > ZnTPP(Ph)₄(CH₃)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)₄X₄ (X = Br and CN) relative to ZnTPP(Ph)₄(CH₃)₄ and follow the order: ZnTPP(Ph)₄(CN)₄ > ZnTPP(Ph)₄Br₄ > ZnTPP(Ph)₄(CH₃)₄ \leq ZnTPP which is approximately in line with an increase in anodic shift of their first ring redox potentials

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