

Redox reactivity of pyri(mi)dinyl-based porphyrins

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Extending the π -conjugation of aromatic molecules, in particular porphyrinoids, via C-C or C-N coupling(s) with peripheral aromatic fragment(s) has been the focus of numerous researches over the last two decades [1]. Indeed, C-C/C-N fusion of one or several hydrocarbon(s) or aromatic heterocycle(s) onto the porphyrin periphery forces the porphyrin core and the substituent to be coplanar, that enhances the electronic communication between both fragments. π -extended porphyrins display important changes in their optical and electrochemical properties such as decrease of the HOMO/LUMO gap, bathochromic shift in their absorption/emission spectra, large absorption and fluorescence in the NIR range [2]. Nowadays, π -extended C-C/C-N linked porphyrins are commonly obtained using toxic and/or expensive chemicals, often under harsh conditions. Due to the extension of the conjugation path, the oxidation potential decreases which may lead to over-oxidation during the fusion process.

In this work, the (electro)chemical oxidation of original pyri(mi)dinyl-porphyrins will be presented affording the C-N fused (bis)pyri(mi)dinium derivatives in a stepwise manner [3a,b]. The resulting pyridinium derivatives exhibit important changes in their physico-chemical properties (NMR, UV-vis., CV) as compared to their initial unfused precursors. The mono- and bis-pyrimidinium-porphyrins are not stable and evolve towards the original *meso*, β -fused thiazinamine-porphyrins [3c].

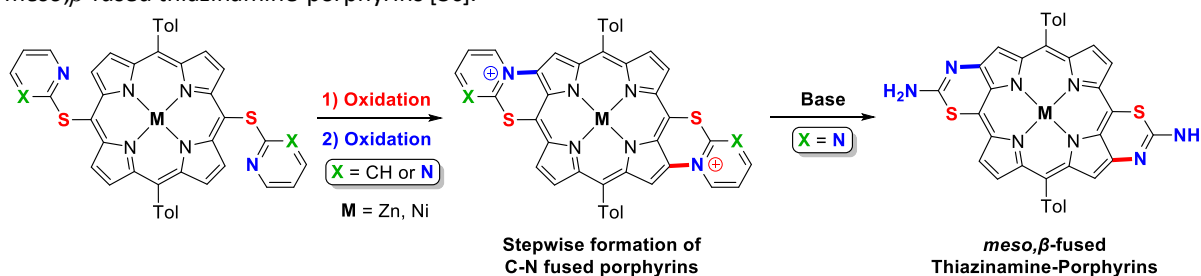


Figure: Oxidative C-N fusion of *meso*-Pyri(mi)din-2-ylthio-Porphyrins.

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