

π -Extension of Ni(II) *meso*-(Pyridin-2-ylthio)Porphyrins

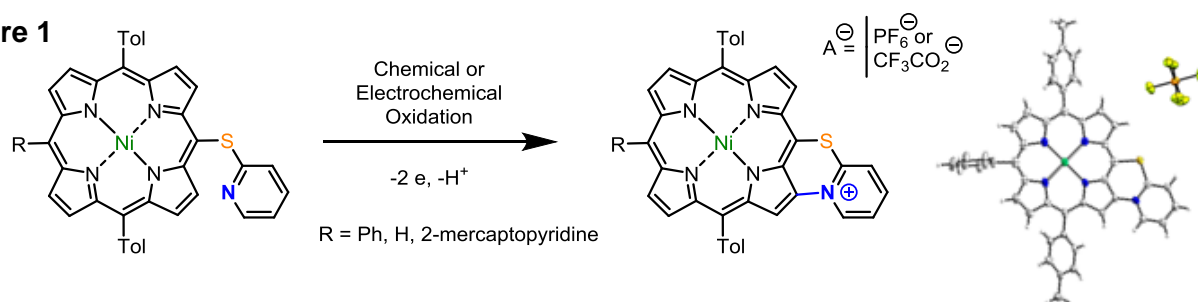
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Porphyrins provide an extremely flexible synthetic scaffold for numerous applications such as artificial photosynthesis, photodynamic therapy, molecular recognition, oxidation/reduction catalysts and molecular materials¹. The fusion of one or several 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. This implies important changes in the optical and electrochemical properties of the fused porphyrin compared to the parent porphyrin core such as decrease of the HOMO/LUMO gap, bathochromic shift in its absorption/emission spectra and large absorption and fluorescence in the NIR range^{2, 3}. For this reason, π -extension of porphyrins has attracted much attention over the last two decades owing to their potential applications in near infrared electroluminescence displays, non-linear optical materials, photodynamic therapy, photovoltaic solar cells and molecular materials^{2,4}. Nowadays, π -extended C-C linked porphyrins are commonly obtained using toxic and/or expensive chemicals, often under harsh conditions^{3,5}. 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, we present the mild and selective chemical and electrochemical synthesis of new π -extended porphyrins generated via intramolecular oxidative C-N coupling of peripheral pyridinyl fragment(s) with the porphyrin core. As compared to their precursors, these fused pyridinium-porphyrins exhibit higher oxidation potential that prevents their over-oxidation.

Figure 1



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