

Electrochemistry and Protonation of Open-Chain Pentapyrroles and Sapphyrins with Highly Electron-Withdrawing *meso*-Substituents

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ABSTRACT

A series of open-chain pentapyrroles and sapphyrins with highly electron-withdrawing *meso*-tetraaryl groups were synthesized and characterized as to their electrochemistry and protonation reactions in nonaqueous media. The chemical conversion of pentapyrroles to sapphyrins upon oxidation in acid media is known but it was not known if sapphyrins could be electrosynthesized from pentapyrroles under the appropriate solution conditions. This was investigated in the present study which compares the redox behavior and acid-base properties of pentapyrroles to that of sapphyrins having the same *meso*-substituents. The investigated compounds were each characterized by UV-vis and ¹H NMR spectroscopy, mass spectrometry and electrochemistry, in addition to spectroelectrochemistry. Structures of the investigated compounds are shown in **Chart 1** and are represented as (Ar)₄PpyH₃ and (Ar)₄SapH₃.

Cyclic voltammetry was used to measure redox potentials and spectroelectrochemistry was used to monitor the products of each redox reaction. The protonation processes were monitored by UV-vis absorption spectroscopy as protons were added to the investigated compounds in the form of trifluoroacetic acid (TFA). Equilibrium constants were calculated using both the Hill equation and the Mole Ratio method. The electrochemical data, the protonation constants and previous reported mechanisms for reduction and oxidation of pentapyrroles and sapphyrins with other *meso*-tetraaryl groups were then analyzed as a function of the solvent properties and *para*-substituents on the four phenyl rings of compounds in the two series.

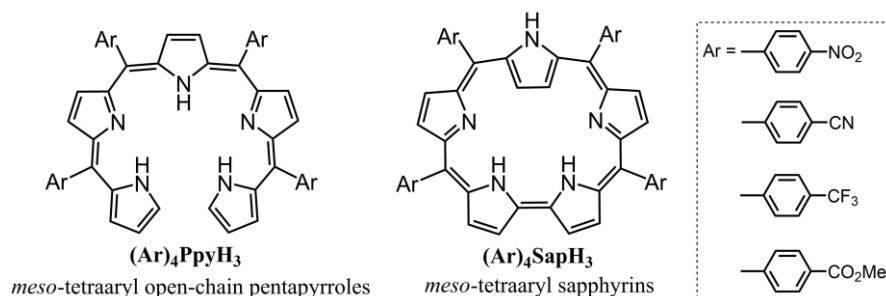


Chart 1