

Title: Supramolecular complexes of oxoporphyrinogens with organic molecules

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Abstract:

Oxoporphyrinogens are flat macrocyclic molecules possessing binding and protonation sites, and capable of light absorption in the visible region. These properties are prerequisites for a colorimetric molecular sensor, i.e. a specific detector of other molecules in the sample. In this work, we studied chromic properties of three oxoporphyrinogens, **OxP** and its partially (**Bz₂OxP**) and fully (**Bz₄OxP**) N-benzylated derivatives. Their colorimetric response to organic acids is caused by protonation and subsequent formation of supramolecular host-guest complex. We have shown that colorimetric sensitivity is highest for **OxP** and gradually weakens for **Bz₂OxP** and **Bz₄OxP** since the N-benzylation blocks the central binding sites, decreasing binding affinity of the oxoporphyrinogens. Furthermore, solvatochromic response of the oxoporphyrinogens to varying solvent polarity showed similar sensitivity decrease in **Bz₂OxP** and **Bz₄OxP**. The chromic and binding properties were studied by UV/vis and NMR spectroscopy, host-guest binding models were applied to describe the formation of oxoporphyrinogen-acid complexes.

In NMR spectra of protonated **OxP** and **Bz₂OxP**, we detected several dynamic processes, manifested as chemical exchange, such as prototropic tautomerization (i.e. change of the protonation site) or rotation of bulky side groups in **Bz₂OxP**. These processes were observed at different temperatures and acid concentrations, the corresponding transition rate coefficients were obtained by fitting of the NMR exchange lineshapes. In protonated **Bz₂OxP**, the effect of temperature obeys the Eyring equation, and the effect of acid concentration has been modeled using a kinetic model derived from competitive host-guest binding.

This thesis presents detailed mechanism of color changes in **OxP**, **Bz₂OxP** and **Bz₄OxP** and confirms potential application as colorimetric sensors in nonpolar media. Our NMR study of dynamic processes in the oxoporphyrinogens contributes to understanding the concentration dependence of transition rate coefficients, which is always system-specific. The presented models can be applied to a wide range of dynamic systems.

Keywords: oxoporphyrinogens, supramolecular complexes, colorimetric sensors, dynamic molecular processes