Novel routes for the modification of iron porphyrins.

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Streszczenie

The effects of unconventional modifications of iron tetraarylporphyrins on their electronic structure and chemical properties were examined. The alterations included the β(*meso*)-substitution or an oxygen atom insertion into an iron–nitrogen bond. The profound transformation of porphyrin to 2-pyridiniumylporphyrin, isoporphyrin or porphodimethene occurred in reactions involving iron porphyrin in highly-oxidized states and pyridine. Addition of 2,4,6-collidine generated iron porphyrin N-oxides. The 2-hydroxy substituted tetraphenylporphyrin (a hybrid-type ligand) coordinates using a tetranitrogen macrocyclic center and an ionized hydroxy group of the periphery to form the cyclic trimer $[(2\text{-O–TPP})Fe(III)]_3$. The seven pyrrole protons of (2-X-TPP)Fe(III)Cl and $[(2\text{-X–TPP})Fe(III)(CN)_2]$ provided the direct probe of the spin density distribution around the porphyrin macrocycle as determined by ^{1}H-NMR. Studies on the controlled modification of the tetraarylporphyrin periphery also included a symmetrical modification of a single pyrrole ring to obtain iron(III) quinoxalinoporphyrin characterized by the less common $(d_{xz}d_{yz})^4(d_{xy})^1$ low-spin ground electronic state of the bis-cyanide derivative $[(QTPP)Fe(III)(CN)_2]^-$.

Słowa kluczowe

Iron porphyrins, Cation radicals, NMR

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