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Electrochemical and Spectroscopic Properties of Cu(II) β-Nitro *meso*-Tetra(pentafluorophenyl)porphyrins

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Abstract: Some electrochemical and spectroscopic properties of the copper(II) derivatives of β-unsubstituted, β-mono-, β-di- and β-tri-substituted *meso*-tetra(pentafluorophenyl)porphyrins are presented. The red-shift observed on the bands of the optical spectra, and the value of the first and second reduction potentials of these compounds depend on the number of nitro substituents on the porphyrin macrocycle.

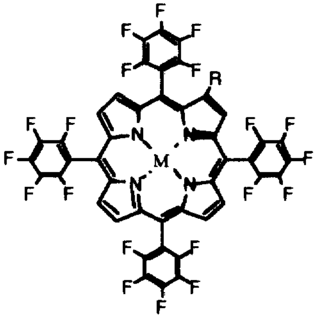
The β-functionalization of *meso*-tetraphenylporphyrins is of considerable chemical interest since many properties of the porphyrin macrocycle can be altered by small changes in the substituents. For example it has been observed[1] that the interaction of the β-substituents and the meso-aryl moiety in β-substituted *meso*-tetraphenylporphyrins leads to a deviation from planarity of the porphyrin macrocycle, which affects its spectroscopic characteristics and chemical behavior. The nitration of the porphyrin macrocycle is of special interest since the nitro groups are very versatile and can be easily converted into several other functional groups.[2] The interesting photophysical properties of β-nitro *meso*-tetraphenylporphyrin derivatives have been reported.[3] To our knowledge the corresponding properties of the fluorinated phenyl derivatives have not yet been reported.

Nitration of the *meso*-tetra(pentafluorophenyl)porphyrin (**1a**) was achieved with $Cu(NO_3)_2$ or with $Zn(NO_3)_2$ in acetic anhydride.[4] A mixture of the mono-nitro (**2**), di-nitro (**3**, **4**) and tri-nitro (**5**) compounds was obtained in quantitative yield. The products obtained were separated by thin layer chromatography (TLC). However, compounds **3**, **4** and **5** are still a mixture of isomers, non-separable by TLC. The products were identified by mass spectrometry, elemental analysis, UV-Vis spectroscopy and ^{1}H-NMR [of the free-base, Zn(II) and Ni(II) analogs]. The red shifts observed on the Soret (B) and Q bands of the products depend on the number of nitro substituents on the porphyrin macrocycles (Table 1). The electrochemical data of the synthesized compounds are also given in Table 1. The reduction potentials were obtained by cyclic voltammetry at a platinum electrode and were measured against a saturated calomel electrode. All data were referenced against the ferrocene/ferrocinium system (530 mV vs. SCE). We were only able to obtain the oxidation potentials for porphyrin **1a** ($E^{1/2}$oxid1 = 0.890 V and $E^{1/2}$oxid2 = 1.230 V). For all investigated compounds two reversible reduction processes were observed. As expected, both the first and the second reduction potentials depend strongly upon the number of nitro substituents on the porphyrin macrocycle. From a Hammett plot of the reduction potentials versus σ^+ we obtained an electrochemical reaction constant ρ of 0.28 for the first reduction potential and a ρ-value of 0.34 for the second reduction potential. These data indicate that the second reduction potential is slightly more sensitive to changes in the electronic nature of the porphyrin macrocycle. Thus the difference between the first and second reduction potentials decreases as the number of nitro substituents increases.

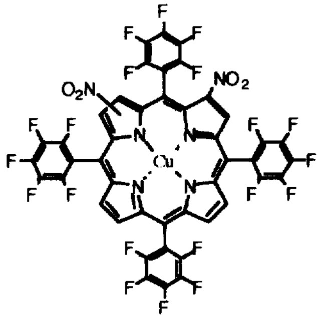
Work is underway in our laboratories to fully characterize the zinc(II) and niquel(II) complexes of all the isomers obtained from the nitration of *meso*-tetra(pentafluorophenyl)porphyrin (**1a**).

Table 1. Electrochemical and Spectroscopic data of the synthesized porphyrins (solvent: CH_2Cl_2; supporting electrolyte: TBATFB, 0.1 M).

Compound	$E^{1/2}$red1 (V)	$E^{1/2}$red2 (V)	ΔE (V)	$\Sigma\sigma^+$	B λ_{max} (nm)	Q1, Q2 λ_{max} (nm)	Absorption Q1/Q2
1a	-1.285	-1.710	0.425	0	411	506, 535	5.681
1b	-1.395	-1.820	0.425	0	409	535, 570	2.333
2	-1.020	-1.340	0.320	0.79	415	542, 588	1.312
3	-0.845	-1.150	0.305	1.58	424	550, 594	1.464
4	-0.870	-1.185	0.315	1.58	422	549, 596	0.868
5	-0.675	-0.970	0.295	2.37	429	555, 599	1.235



1a: M=2H, R=H
1b: M=Cu, R=H
2: M=Cu, R=NO_2



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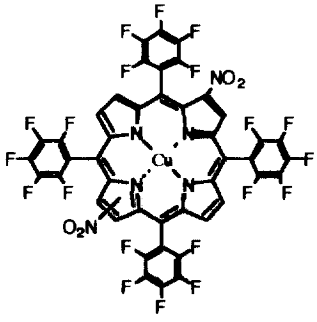

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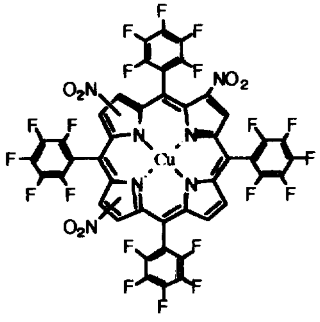

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