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Preparation of *meso*-Tetra(4-galvinolphenyl)porphyrin — A Building Block for Molecular Magnetic Materials

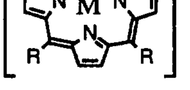
David A. Shultz,* David A. Knox, Larry W. Morgan, Kay Sandberg, and Gregory N. Tew
Department of Chemistry, Box 8204
North Carolina State University
Raleigh, North Carolina 27695-8204

Abstract: The synthesis and oxidative electrochemistry of a free-radical substituted metalloporphyrin are described. The porphyrin is prepared in four steps in good yield. Oxidation at a platinum electrode shows the molecule undergoes five reversible one-electron transfers to a stable pentaradical.

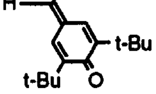
Introduction

Recently, there has been considerable interest in organic-based and organic-containing magnetic materials: molecular crystals, charge transfer complexes, and polymers.[1] The use of metals in the design of molecular magnetic materials is attractive for a number of reasons. Metals are not only an undeniably excellent source of spin, but their coordination spheres can provide a rational approach to three-dimensionality. Four different approaches to metal-containing molecular systems have produced materials showing spontaneous magnetization: one-dimensional charge-transfer complexes prepared by Miller and coworkers,[2] one-dimensional ferrimagnetic chains by Kahn et al,[3] one-dimensional metal-radical complexes by Gatteschi and coworkers,[4] and three-dimensional mixed-metal assemblies by Matsumoto and Okawa.[5] We feel that the radical/metal approach of Gatteschi and coworkers offers considerable potential. They developed molecular magnetic materials using substituted nitronyl nitroxides and transition metals. A limitation of nitronyl nitroxides as paramagnetic ligands is that they bind to metals in a number of geometries and therefore it is difficult to anticipate or design specific magnetic properties. We wish to prepare new classes of paramagnetic ligands with well defined binding geometries. Because we want to prepare room-temperature stable materials, the paramagnetic building blocks must be stable. Currently, we are using tetraarylporphyrin cation radicals[6] and substituted galvinoxyls.[7]

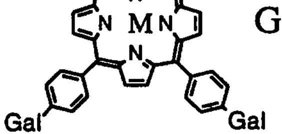
These two paramagnetic species can be combined to give the pentaradical **Gal$_4$TPPM$^{+\bullet}$**, shown below. This molecule offers several possibilities for preparing very high spin molecules and materials, e.g., sandwich complexes,[8] cofacial structures and bridged dimers,[9] and extended chain structures.[10]



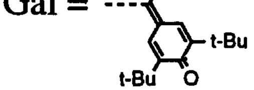
METALLOPORPHYRIN
RADICAL CATION



GALVINOXYL



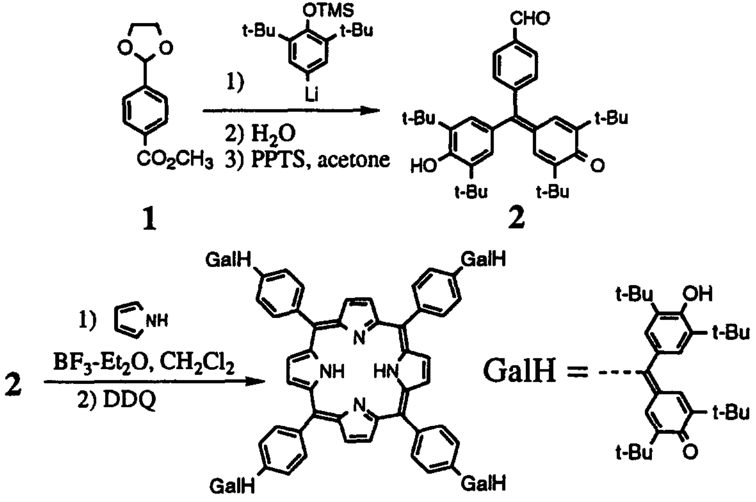
Gal$_4$TPPM$^{+\bullet}$



The galvinoxyls are attached to the porphyrin-phenyl groups at a node, and therefore negligible spin-spin communication among them is expected. However, spin-spin comunication might be induced by one-electron oxidation of the tetraphenylporphyrin core. High-spin coupling is expected based on the topology of the system.[11] The spin-spin interaction will be attenuated by torsion of the phenyl groups, but nonetheless this motif offers exciting possibilities. The metals can be chosen solely for their propensity to bind bridging ligands or for an ability to add electrons to the system. For the latter case there is precedent for ferromagnetic interaction between metal-based spins and porphyrin-based spins.[12] Herein we describe the preparation of **$GalH_4TPPH_2$**, and voltammetry of its zinc complex.

Results and Discussion

$GalH_4TPPH_2$ was prepared in four steps starting with ketal-protection of commercially available methyl 4-formylbenzoate to yield compound **1**.[13] Reaction of **1** with 4-lithio-2,6-di-*t*-butylphenol trimethylsilyl ether,[14] followed by removal of trimethylsilyl groups and deketalization yields **2** in over 90% yield. Porphyrin formation[15] completes the synthesis.



1

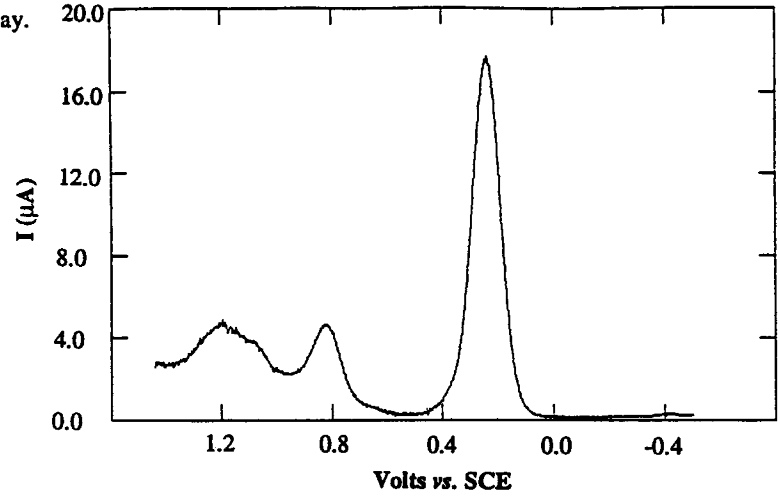
2

2

$GalH_4TPPH_2$

Metallation[16] of **$GalH_4TPPH_2$** using zinc acetate in boiling chloroform/ethanol was followed by UV-visible spectrophotometry. The four visible porphyrin bands gave way to new metalloporphyrin Q bands (see experimental section).

Oxidation. Galvinols of **$GalH_4TPPZn$** were converted to galvinoxyls by stirring with PbO_2.[17] This solution was transferred to an electrochemical cell, and cyclic and differential pulse voltammograms were recorded. A typical differential pulse voltammogram is shown below. These experiments show a reversible redox couple near +220 mV and a reversible couple near +810 mV vs. SCE. We attribute the former couple to the galvinoxyl radical and its anion,[18] and the latter to oxidation of the tetraarylporphyrin core.[6] Identical voltammograms can be recorded starting from the tetraanion prepared by stirring **$GalH_4TPPZn$** and NaH in dimethylformamide at 0°C. Oxidation of the porphyrin cation radical and irreversible oxidation of the galvinoxyls occurs at potentials greater than 1 V. Since the tetraaryl-porphyrin oxidation is well removed from the irreversible galvinoxyl oxidation, stable pentradicals may be prepared by bulk electrolysis. Efforts to prepare and characterize these species are underway.



Conclusions

Tetra-(4-galvinolphenyl)porhyrin has been prepared in good yield. The free-base porphyrin can be metallated under the same conditions used for tetraphenylporphyrin metallation. Electrochemical studies of the zinc complex show that this molecule can undergo oxidation to yield a stable pentaradical.

Experimental

Melting points were determined on a Fisher melting point apparatus and are uncorrected. Solvent distillations, synthetic procedures, and electrochemistry were carried out under an argon atmosphere. Tetrahydrofuran was distilled from sodium benzophenone-ketyl prior to use. Methylene chloride was distilled from calcium hydride. NMR spectra were recorded on a Varian 300 MHz spectrometer using deuterochloroform as solvent, and referenced to protiochloroform at 7.26 ppm for ^{1}H spectra and 77.0 ppm for ^{13}C spectra. UV-visible spectra were recorded on a Hewlett-Packard 8452 spectrophotometer. Electrochemical experiments were performed with a EG&G PAR Model 273 potentiostat. Methylene chloride or dimethylformamide (Aldrich, anhydrous) solutions for electrochemistry were 1.5 mM in porphyrin and 100 mM in tetrabutylammonium hexafluorophosphate electrolyte. Pt disk and Pt wire served as the working and auxiliary electrodes, respectively, and the reference electrode was saturated calomel.

GalH$_4$TPPH$_2$. The porphyrin was prepared in 30-40% yield using the method of Lindsey.[15] The chromatographic workup described worked beautifully, and the fraction containing **GalH$_4$TPPH$_2$** was collected as a rust-colored solution. The solid produced by evaporation is purple. ^{1}H NMR: 8.96, s, 8H (pyrrole-H); 8.34, d, J = 8 Hz, 8H (ArH); 7.74, d, J = 8 Hz, 8H (ArH); 7.58, d, J = 2 Hz, 4H (quinoid-H); 7.52, d, J = 2 Hz, 4H (quinoid-H); 7.40, s, 8H (phenol-ArH); 5.67, s, 4H (-OH); 1.54, s, 72H (phenol *t*-Bu-H); 1.47, s, 36H (quinoid *t*-Bu-H); 1.41, s, 36H (quinoid *t*-Bu-H); -2.65, s, 2H (NH). ^{13}C NMR: 186.20, 157.42, 155.79, 147.27, 146.74, 142.66, 141.33, 135.52, 133.92, 132.78, 132.47, 131.81, 130.50, 129.19, 119.80, 35.44, 34.56, 30.39, 29.76, 29.61. Uv-vis (CH$_2$Cl$_2$): 280, 426, 518, 554, 592, 648 nm. mp. > 300°C. Anal. calcd. C: 83.65%; H: 8.34%; N: 2.44%, found C: 82.95%; H: 8.27%; N: 2.37%.

GalH$_4$TPPZn. **GalH$_4$TPPH$_2$**, (100 mg, 44 μmol) and zinc acetate dihydrate (14 mg, 65 μmol) were added to a solution of 10 ml chloroform and 5 ml ethanol. The mixture was refluxed under argon. After two hr. the reaction mixture was cooled, an aliquot removed, diluted with methylene chloride, and a UV-vis spectrum was recorded. The spectrum showed only the characteristic α and β metalloporphyrin bands in the visible region. The reaction mixture was evaporated, dissolved in a minimum of methylene chloride, and passed through a 1" X 3" florosil column, eluting with methylene chloride. The colored fraction was collected and evaporated, yielding a purple solid. ^{1}H NMR: 9.03, s, 8H (pyrrole-H); 8.32, d, *J* = 8 Hz, 8H (ArH); 7.71, d, *J* = 8 Hz, 8H (ArH); 7.58, broad s, 4H (quinoid-H); 7.50, broad s, 4H (quinoid-H); 7.39, s, 8H phenol-ArH); 5.64, s, 4H (-OH); 1.57, s, 72H (phenol *t*-Bu-H); 1.45, s, 36H (quinoid *t*-Bu-H); 1.39, s, 36H (quinoid *t*-Bu-H). ^{13}C NMR: 186.23, 157.56, 155.80, 150.15, 147.29, 146.75, 143.40, 141.14, 135.57, 133.81, 132.88, 132.49, 131.92, 130.38, 129.20, 120.77, 35.48, 34.61, 30.43, 29.81, 29.65. Uv-vis (CH_2Cl_2): 278, 432, 556, 598 nm. mp. > 300°C.

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