

Short Note

## Copper 5,10,15,20-Tetra(*N*-ethyl-3-carbazolyl) Porphyrin

Cynthia P. Tidwell <sup>1,\*</sup>, L. Dalila Fondren <sup>1</sup> and David E. Nikles <sup>2</sup>

<sup>1</sup> Department of Biology, Chemistry, and Mathematics, University of Montevallo, UM Station 6480, Montevallo, Alabama, 35115, USA

<sup>2</sup> Department of Chemistry, The University of Alabama, UA Box 870336, Tuscaloosa, Alabama, 35487, USA

\* Author to whom correspondence should be addressed; E-Mail: tidwellc@montevallo.edu.

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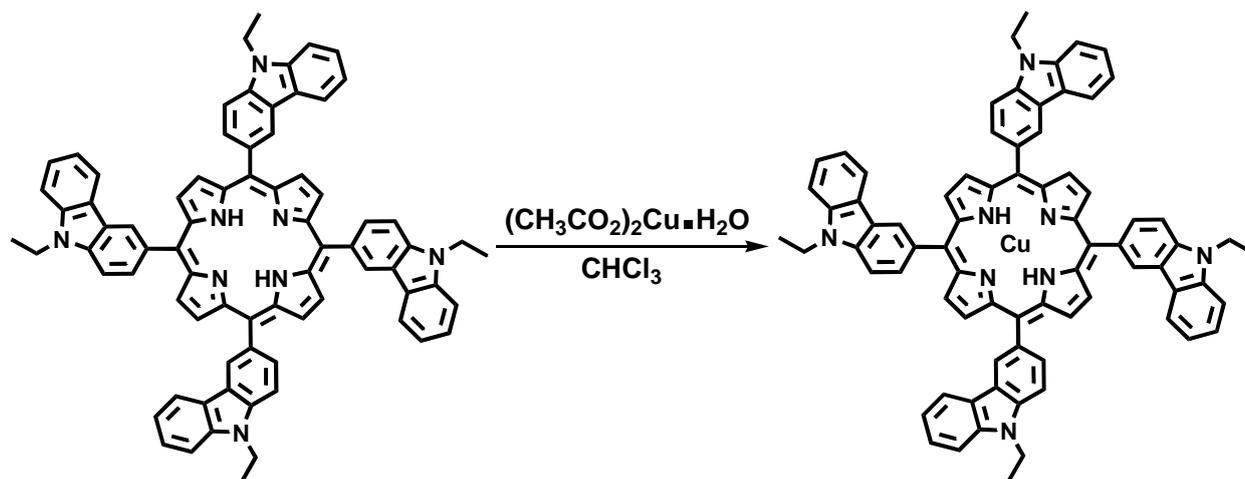
**Abstract:** The copper complex of 5,10,15,20-Tetra(*N*-ethyl-3-carbazolyl) porphyrin was synthesized and characterized by electronic absorption spectrophotometry and cyclic voltammetry. The spectral data were in agreement with the proposed structure. The copper complex exhibited a shift in the Soret band in comparison to the non-metallated porphyrin and the extinction coefficient for the Soret band was on the order of  $10^5 \text{ cm}^{-1}\text{M}^{-1}$ . Trends observed in the oxidation and reduction potentials were consistent with the nature of the porphyrin. That is, the electron donating group in 5,10,15,20-tetra(*N*-ethyl-3-carbazolyl) porphyrin enhances oxidation and inhibits reduction.

**Keywords:** porphyrin; chromophore; metal complex

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### Introduction

Porphyrins are of interest in many areas of study including photodynamic cancer therapy, optical data storage, sensors, and solar energy [1-5]. The focus of this paper is to report the synthesis, electronic absorption spectroscopy, and cyclic voltammetry of the copper complex of 5,10,15,20-tetra(*N*-ethyl-3-carbazolyl) porphyrin, TECP.



## Experimental Section

### Chemicals and Reagents

Reagents and solvents used in the synthesis and metallation of TECP, NMR measurements, and UV-vis were purchased from Aldrich Chemical Company and used as received. Methylene chloride used in cyclic voltammetry experiments was distilled over calcium hydride before use. Tetrabutylammonium tetrafluoroborate was purchased from Fisher Scientific Company and used as received.

### Instrumentation

Ultraviolet-visible (UV-vis) absorption spectra were recorded on a Hewlett Packard 8451A spectrophotometer. Cyclic voltammograms (CV) were recorded using a computer linked EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273 equipped with an IR compensator and model 270 Electrochemical software. The CVs were obtained in a four-necked cell with a platinum working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A capacitor (0.1  $\mu\text{F}$ ), was connected between the counter electrode and the reference electrode to reduce background noise. The porphyrin solutions were  $1 \times 10^{-3}$  M in 0.1 M methylene chloride solutions of tetrabutylammonium tetrafluoroborate. Potentials were reported versus a S.C.E. and not corrected for liquid junction potentials. Deaeration of the solution was achieved by passing a stream of nitrogen through the solution. The platinum working electrode was cleaned with solvent, using a lint free wipe, between each run and polished periodically.

### Synthesis

*5,10,15,20-Tetra(N-ethyl-3-carbazolyl) Porphyrin*: TECP was synthesized as reported previously [6]. The structure was confirmed using  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, UV-Vis and high resolution mass spectrometry. UV ( $\text{CHCl}_3$ ) [ $\lambda, \text{nm}$  ( $\epsilon$ ,  $\text{cm}^{-1}\text{M}^{-1}$ ): 433( $2.8 \times 10^5$ ), 523( $1.3 \times 10^4$ ), 562.5( $1.1 \times 10^4$ ), 654.5( $5.6 \times 10^3$ ).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.97 (s, 4H), 8.89 (s, 8H), 8.37(d, 4H,  $J = 8.1$  Hz), 8.19 (d, 4H,  $J = 7.8$  Hz), 7.75 (d, 4H,  $J = 8.2$  Hz), 7.58 (m, 8H), 7.28 (t,  $J = 7.8$  Hz), 4.63 (q,  $J = 7.1$ ), 1.68 (t,  $J = 7.0$ ), -2.4 (s).  $^1\text{H}$  NMR (360 MHz, Acetone- $d_6$ ),  $\delta$  (ppm): 9.03 (s), 8.93 (s),

8.40 (d,  $J = 8.4$  Hz), 8.32(d,  $J = 7.6$  Hz), 7.99 (d,  $J = 8.4$  Hz), 7.76 (d,  $J = 8.3$  Hz), 7.58 (t,  $J = 7.7$  Hz), 7.27 (t,  $J = 7.5$  Hz), 4.76 (q,  $J = 7.1$ ), 1.65 (t,  $J = 7.0$ ), -2.4 (s). HRMS-FAB ( $m/z$ ): calcd for  $C_{76}H_{59}N_8$ : 1083.486 a.m.u.; observed: 1083.487 a.m.u.

*Copper 5,10,15,20-Tetra(N-ethyl-3-carbazolyl) Porphyrin.* The copper 5,10,15,20-Tetra(*N*-ethyl-3-carbazolyl) porphyrin was prepared using chromatographed TECP (0.2002 g,  $1.848 \times 10^{-4}$  mol), in approximately 50 mL of boiling chloroform. To this solution a saturated solution of copper (II) acetate hydrate in 3 mL of methanol was added. After 1 minute of refluxing the reaction mixture was found to have a  $\lambda_{max}$  of 429 nm. This shift in the electronic absorption spectrum indicated the completion of the reaction. The reaction mixture was rotavaped to dryness, rinsed with methanol, and filtered giving 0.2189 g ( $1.912 \times 10^{-4}$  moles) of crude Cu(II)TECP. The Cu(II)TECP was purified using a silica gel column with  $CHCl_3$  as the eluent coming off as a brilliant red band. For 0.1093 g crude compound chromatographed, 0.0253 g of pure compound was obtained. Thus, for the overall reaction 0.0507 g,  $4.43 \times 10^{-5}$  moles, of pure CuTECP was obtained, giving a yield of 23.9%. UV-vis Data [ $\lambda$ ,nm ( $\epsilon$ ,  $cm^{-1}M^{-1}$ )],  $CHCl_3$  429( $2.4 \times 10^5$ ), 545( $1.2 \times 10^4$ ), 583( $3.4 \times 10^3$ ).

## Results and Discussion

In the electronic absorption spectra of the metallated porphyrin a shift in the Soret band and the disappearance of at least one of the Q bands is expected and observed. This disappearance is due to the increased symmetry acquired by the porphyrin with introduction of a metal ion to the ring. The extinction coefficient for the Soret band are on the order of  $10^5 cm^{-1}M^{-1}$ .

CuTECP undergoes two successive one-electron oxidations at 0.875 V and 1.248 V vs. S.C.E. A single electron reduction of CuTECP is observed at -1.29 V vs. S.C.E. These values for the electro-oxidation and reduction of CuTECP correspond extremely well with what is reported in the literature for CuTPP. It is reported that CuTPP in benzonitrile with 0.1 M  $nBu_4NClO_4$  undergoes two, one electron oxidations at 0.99 V and 1.33 V vs. S.C.E. [7]. A reduction of CuTECP was observed at -1.20 V vs. S.C.E. This corresponds to a reduction of CuTPP in THF-DMF solvent reported to occur in at -1.20 V vs. S.C.E. [8,9].

## Conclusions

All data observed for the copper complex of TECP follow trends expected when compared to the TPP complexes.

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