# Continuous-Wave and Pulse EPR Study of the Cu(II) Complex of N-Confused Tetraphenylporphyrin: Direct Observation of a σ Metal-Carbon Bond

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**Figure S1:** Schematic representation of the atomic orbitals involved in forming the molecular orbitals described in Eq. 1. The phase resulting in the anti-bonding orbitals is not taken into account in this representation.



**Figure S2:** Difference  $A_x - A_y$  as a function of the  $3d_{z^2}$  contribution,  $c_2^2$  calculated using Eq. 8 under the normalization condition  $c_1^2 + c_2^2 = 1$ . The dashed line describes the experimentally found maximum difference.

Quantity	N( <sup>4</sup> S)	$N^{-1}(^{3}P)$	$\frac{1000 \text{ value qual}}{C(^{3}\text{P})}$	$C^{-1}(^4S)$
$ ho_{ m 2s}(0)^{a}$	4.7687	4.4880	2.7699	2.5146
$\langle r^{-3} \rangle_{2p}^{a}$	3.0993	2.3669	1.6912	1.2350

Table S1: Numerical values of relevant quantities

<sup>*a*</sup> All values are given in atomic units. Consequently, in order to calculate hyperfine couplings in MHz, the multiplication factor  $1/a_0^3 = 6.74833 \times 10^{30} \text{ m}^{-3}$  has to be included in Eq. 10 and Eq. 11.

## **Calculation of Overlap Integrals**

$$\langle \Phi_{a1} | \sigma_{N13} \rangle = c_1 \langle d_{x^2 - y^2} | \sigma_{N13} \rangle + c_s \langle 4s | \sigma_{N13} \rangle = c_1 \sqrt{2} \langle d_{x^2 - y^2} | -\sigma_x(1) \rangle + c_s \sqrt{2} \langle 4s | -\sigma_x(1) \rangle = c_1 \sqrt{2} \Big[ n_{N1,3} \langle d_{x^2 - y^2} | -2p_x \rangle + \sqrt{1 - n_{N1,3}^2} \langle d_{x^2 - y^2} | -2s \rangle \Big] + c_s \sqrt{2} \Big[ n_{N1,3} \langle 4s | -2p_x \rangle + \sqrt{1 - n_{N1,3}^2} \langle 4s | -2s \rangle \Big]$$
(S1)

$$\langle \Phi_{a1} | \sigma_{N2} \rangle = c_1 \langle d_{x^2 - y^2} | \sigma_{N2} \rangle + c_s \langle 4s | \sigma_{N2} \rangle = c_1 \langle d_{x^2 - y^2} | -\sigma_{y'}(2) \rangle + c_s \langle 4s | -\sigma_{y'}(2) \rangle = c_1 \Big[ n_{N2} \langle d_{x^2 - y^2} | -2p_y \rangle + \sqrt{1 - n_{N2}^2} \langle d_{x^2 - y^2} | 2s \rangle \Big] + c_s \Big[ n_{N2} \langle 4s | -2p_y \rangle + \sqrt{1 - n_{N2}^2} \langle 4s | 2s \rangle \Big]$$
(S2)

$$\langle \Phi_{a1} | \sigma_{C} \rangle = c_{1} \langle d_{x^{2}-y^{2}} | \sigma_{C} \rangle + c_{s} \langle 4s | \sigma_{C} \rangle = c_{1} \langle d_{x^{2}-y^{2}} | \sigma_{y}(4) \rangle + c_{s} \langle 4s | \sigma_{y}(4) \rangle = c_{1} \left[ n_{C} \langle d_{x^{2}-y^{2}} | 2p_{y} \rangle + \sqrt{1 - n_{C}^{2}} \langle d_{x^{2}-y^{2}} | 2s \rangle \right] + c_{s} \left[ n_{C} \langle 4s | 2p_{y} \rangle + \sqrt{1 - n_{C}^{2}} \langle 4s | 2s \rangle \right]$$
(S3)

The necessary overlap integrals between metal and ligand AO used in the present analysis are given in Table S2 for three different cases of ligand valence states: 1. all atoms were considered to be neutral, 2./3. a doubly positively charged copper atom with two negatively charged ligand atoms (either N<sub>1,3</sub> or N<sub>2</sub> and C).

Group overlap	$ig \langle \Phi_{_{ m a1}} ig   \sigma_{_{ m N13}} ig  angle$	$ig \langle \Phi_{_{\mathrm{a}1}} ig   \sigma_{_{\mathrm{N}2}} ig  angle$	$\langle \Phi_{_{\mathrm{a}1}} ert \sigma_{_{\mathrm{C}}}  angle$
	$ -2s\rangle  -2p_x\rangle$	$ 2s\rangle  -2p_y\rangle$	$ 2s\rangle$ $ 2p_y\rangle$
$Cu(^{2}S)$	$N_{1,3}(^{4}S)$	N <sub>2</sub> ( <sup>4</sup> S)	$C(^{3}P)$
$\left\langle d_{x^2-y^2} \right $	0.0703 0.0707	0.0752 0.0736	0.0844 0.0768
$\langle 4s  $	-0.2835 -0.1835	0.2939 0.1860	0.3728 0.2483
$Cu^{+2}(^{2}D)$	$N_{1,3}(^{4}S)$	$N_2^{-1}({}^3P)$	<b>C</b> <sup>-1</sup> ( <sup>4</sup> <b>S</b> )
$\left\langle d_{x^2-y^2} \right $	0.0433 0.0539	0.0471 0.0519	0.0528 0.0523
$\langle 4s  $	-0.2835 -0.1835	0.3175 0.2821	0.4084 0.3439
$Cu^{+2}(^{2}D)$	$N_{1,3}^{-1}(^{3}P)$	$N_2(^4S)$	<b>C</b> ( <sup>3</sup> <b>P</b> )
$\left\langle d_{x^2-y^2} \right $	0.0434 0.0493	0.0471 0.0573	0.0552 0.0625
$\langle 4s  $	-0.3067 -0.2803	0.2939 0.1860	0.3728 0.2483

**Table S2:** Overlap integrals of atomic orbitals<sup>*a*</sup> for the Cu(II)NCTPP complex.  $R_{N1,N3} = 2.07$  Å,  $R_{N2} = 2.02$  Å,  $R_{C} = 1.96$  Å.

<sup>*a*</sup>The atomic orbitals have been constructed using the expansion coefficients and orbital exponents given in ref 37.

#### **Preparations**

## <sup>13</sup>C-Pyrrole

All experimental details of the pyrrole synthesis were tested with a non-enriched starting material and analyzed in detail in advance.

<sup>13</sup>C-Mucic Acid. U<sup>13</sup>C-D-galactose (2.7 g, 14.5 mmol, Campro Scientific, 99.2 atom percent 13C, 99.9%) was placed in a porcelain crucible. A white suspension was formed upon adding HNO<sub>3</sub> (22 ml, 4.76 N, Merck, p.a.). After stirring at 100 °C during 1 h a thick white-brownish paste was obtained. Water (1 ml) was added, and the covered crucible was kept under stirring at room temperature overnight. The suspension was filtered and washed two times with cold water. Afterwards, the white remainder was dried for 5 h at 80 °C. Yield: 2.2 g, 70 %.

Ammonium <sup>13</sup>C-Mucate. <sup>13</sup>C-Mucic Acid (2.2 g, 10 mmol) was placed in a porcelain crucible, after which water (1.6 ml) was added. NH<sub>4</sub>OH (25 weights %) was added while stirring and the resulting suspension was dried while slowly stirring during night at room temperature. The remainder was dried for 24 h under vacuum, resulting in a beige powder. Yield: 2.49 g, 98%

<sup>13</sup>C-Pyrrole. Glycerol (1.3 ml, Fluka, 87 %) enriched with ammonia and ammonium <sup>13</sup>C-mucate (2.49 g, 9.6 mmol) was added to a 5 ml round bottom flask of a dedicated micro distillation apparatus. The apparatus was flushed with  $N_2$  for 10 min, after which it was heated up to 90 °C using a heat gun. The temperature was kept constant until a stirrable paste was obtained. After this, the stirring speed and the temperature were slowly increased up to 250 °C. Pyrrole was formed on top of an aqueous phase in the collection vessel. The distillation was stopped and the resulting pyrrole was syringed out of the vessel and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 ml, freshly distilled), after which it was dried over NaOH. Finally, the filtrate was dissolved in CH<sub>2</sub>Cl<sub>2</sub> in order to achieve a volume of 100 ml. Yield: 0.249 mg (theoretically calculated, not determined in this run, as subsequently the product was directly used in the synthesis of the ligand. But before, all experimental details were tested with a non-enriched starting material leading to a yield of 0.24 g, 35 %.)

## <sup>13</sup>C-2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrin, <sup>13</sup>C-NCTPPH<sub>2</sub>

To a heated and N<sub>2</sub>-flushed 500 ml flask, benzaldehyde (371.5 mg, 3.5 mmol), CH<sub>2</sub>Cl<sub>2</sub> (230 ml) and <sup>13</sup>C-Pyrrole (248.7 mg, 3.5 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) were added, after which MSA (235.5 mg, 2.45 mmol, Acros, 98 %) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was slowly added during 2 min at room temperature. Upon this, a colour change from yellow to orange/ red to dark-blue/ black can be observed. The reaction mixture was stirred for 30 min at room temperature after which DDQ (699.2 mg, 3.08 mmol, Acros, 98 %) was added. After stirring for 1 min, the reaction was quenched by addition of TEA (991.7 mg, 9.8 mmol, Acros, 98 %). Subsequently, the mixture was filtered, and the remainder washed with CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was passed through a column (basic activity III alumina in CH<sub>2</sub>Cl<sub>2</sub>), which was rinsed with CH<sub>2</sub>Cl<sub>2</sub> (250 ml) containing 1 % TEA. The eluant obtained as a single fraction was evaporated to near dryness. The sample was adsorbed onto 5 g basic acitivity III alumina and then dried in vacuum during 12 h. The adsorbed sample was added on a column (basic activity III alumina in 3:1 hexane/ CH<sub>2</sub>Cl<sub>2</sub>) and eluted with each 120 ml of increasing polarity from 3:1 to 1:1 to 1:2 hexane/ CH<sub>2</sub>Cl<sub>2</sub>. Finally, the column was rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The collected fractions were analyzed by TLC (alumina, 1:1 hexane/ CH<sub>2</sub>Cl<sub>2</sub>) and the NCTPP-containing fractions (starting from 1:2 hexane/ CH<sub>2</sub>Cl<sub>2</sub>) were pooled. After evaporation to dryness, 92 mg of a brown-blue powder was obtained. The product was re-crystallized in 2:1 hexane/ CH<sub>2</sub>Cl<sub>2</sub> and dried in vacuum during 48 h. Yield: 61 mg, 11 %. EIMS: 630.30 ([C<sub>28</sub><sup>13</sup>C<sub>16</sub>N<sub>4</sub>H<sub>30</sub>]), calculated for C<sub>28</sub><sup>13</sup>C<sub>16</sub>N<sub>4</sub>H<sub>30</sub> 630.20 g/mol.

## 2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrinatocopper(II), Cu<sup>II</sup>NCTPP

The following metal insertions were done in a glovebox ( $p_{oxygen} < 5$  ppm,  $p_{water} < 5$  ppm).

Copper(II) acetate (22 mg, 121  $\mu$ mol; Aldrich, 99.999%) was dissolved in THF (30 ml, Fluka, puriss. p.a.). NCTPPH<sub>2</sub> (100 mg, 163  $\mu$ mol) was added as a THF solution (30 ml). After stirring for 20 h at room temperature, the solvent was removed. The extract (4 x 10 ml toluene, Baker, > 99.5 %) was filtered. The volume of the solution was reduced to approx. 15 ml applying low pressure. 10 ml hexane (Fluka, > 99 %) were added, the precipitate was filtered and washed with 6 ml hexane and afterwards dried in vacuum. Yield: 53 mg, 65 %. MALDIMS(+): 676.2 ( $[C_{44}H_{29}N_4Cu]^+$ ), calculated for  $C_{44}H_{28}N_4Cu$  675.161 g/mol.

**2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrinato-63-copper(II)**,  ${}^{63}$ Cu<sup>II</sup>NCTPP. To 63-Copper(II) chloride (6.5 mg, 48.9 µmol) in THF (10 ml, Fluka, puriss. p.a.) NCTPPH<sub>2</sub> (30 mg, 48.9 µmol) was added as a THF solution (10 ml), after which 2,6-Lutidine (20 µl, 171 µmol, Fluka, puriss. p.a.) was added. After stirring for 30 h at room temperature, the reaction mixture was transferred to another vial using a syringe after which the solvent was removed. No further purification steps have been applied, as the paramagnetic purity could be proved by cw EPR spectroscopy.

<sup>13</sup>C-2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrinato-63-copper(II), <sup>13</sup>C-<sup>63</sup>Cu<sup>II</sup>NCTPP. To 63-Copper(II) chloride (6.5 mg, 48.9  $\mu$ mol) in THF (10 ml, Fluka, puriss. p.a.) NCTPPH<sub>2</sub> (32 mg, 50.8  $\mu$ mol) was added as a THF solution (10 ml), after which 2,6-Lutidine (20  $\mu$ l, 171  $\mu$ mol, Fluka, puriss. p.a.) was added. After stirring for 20 h at room temperature, the reaction mixture was transferred to another vial using a syringe after which the solvent was removed. No further purification steps have been applied, as the paramagnetic purity could be proved by cw EPR spectroscopy.

The following procedure applies for Cu<sup>II</sup>NCTPP, <sup>63</sup>Cu<sup>II</sup>NCTPP and <sup>13</sup>C-<sup>63</sup>Cu<sup>II</sup>NCTPP.

Magnetically diluted Cu<sup>II</sup>NCTPP in ZnTPP. Cu<sup>II</sup>NCTPP (1 mg, 1.5  $\mu$ mol) and zinc(II)mesotetraphenylporphine (100 mg, 147  $\mu$ mol, ABCR, ZnTPP) were dissolved in THF (20 ml) and stirred during 2h. After removing the solvent, the obtained microcrystals were carefully ground in order to get a homogenous powder.

A small amount of the powder was filled into an EPR quartz tube, which afterwards was evacuated (2 x  $10^{-6}$  mbar) and then sealed.