Supporting Information

Synthesis and characterization of mono- and dinuclear phenanthroline-extended tetramesityl porphyrin complexes as well as UV-Vis and EPR studies on their one-electron reduced species

Corinna Matlachowski[1] and Matthias Schwalbe[1]*

[1] *Institute of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-St. 2, 12489 Berlin, Germany*; *matthias.schwalbe@hu-berlin.de

Synthesis of copper compounds

2-Nitro-*meso*-tetramesitylporphyrinatocopper(II) (CuTMP-NO$_2$)

This procedure was based on a literature protocol.[1] CuTMP (74 mg, 0.087 mmol) was dissolved in 15 mL DCM in a 100 mL round-bottom flask sealed with a rubber septum. NO$_2$ was generated by the thermal decomposition of Pb(NO$_3$)$_2$ in a schlenk-tube and was transferred in portions of 2 mL by a syringe into the reaction flask. The reaction was monitored with silica TLC (hexane : DCM = 3:2). When all starting material was consumed, the reaction was terminated by flushing with air to remove remaining NO$_2$ gas. After removal of organic solvents under vacuum, the solid residue was suspended in hexane and loaded on a silica column packed with hexane. The product was eluted with a gradient of hexane and DCM (10 - 37.5 % DCM, 7.5 % per 200 mL). CuTMP-NO$_2$ (77 mg, 0.086 mmol, 99 %) was isolated as dark purple solid. The characterization was identical to the literature.

2-Amino-*meso*-tetramesitylporphyrinatocopper(II) (CuTMP-NH$_2$)

This procedure was based upon a literature protocol.[1] CuTMP-NO$_2$ (125 mg, 0.14 mmol) was dissolved in 30 mL dry DCM and 10 mL dry Methanol under argon atmosphere and 120 mg Pd (10% on carbon) was added. Sodium borohydride (75 mg, 1.72 mmol) was added to the solution in small portions. The reaction mixture was stirred for 1 h and all solvent was removed subsequently under reduced pressure. The residue was passed through a plug of celite using DCM as eluent. Due to the instability of the product against photo-oxidation it was used immediately for the following reaction without further purification.

2,3-Dioxo-*meso*-tetramesitylchlorinatocopper(II) (CuTMCO$_2$)

This procedure was based upon a literature protocol.[1] CuTMP-NH$_2$ was dissolved in 20 mL DCM and the solution was illuminated (Bulb light – 250 W) in an open vessel for 48 h. The solvent was removed under reduced pressure and the solid residue purified by column chromatography with a gradient of hexane and DCM. The column was packed with 3:1 mix of hexane : DCM and then eluted with a gradient (25 -70 % of DCM, 7.5 % per 200 mL). CuTMCO$_2$ (80 mg, 0.09 mmol, 65 % based on CuTMP-NO$_2$) was isolated as green powder and characterized according to the literature.

(Pyrazo[5’,6’-*e*]-1’,10’-phenanthroline)[*b*]*meso*-tetramesitylporphyrinato-copper(II) (Cu-1)

This procedure was based on a literature protocol.[1] CuTMCO$_2$ (163 mg, 0.19 mmol) and phendiamine (127 mg, 0.61 mmol) were dissolved in 350 mL dry DCM under argon atmosphere. 0.59 mL trifluoroacetic acid was added and the reaction mixture was heated at reflux overnight. The color of the solution changed from green to dark violet. The reaction mixture was subsequently washed with 5 % aqueous Na$_2$CO$_3$, water and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the product purified with column chromatography. The column was packed with DCM. Unreacted CuTMCO$_2$ was eluted with DCM and with a mixture of 95 % DCM and 5 % methanol a violet band was collected to yield **Cu-1** as dark violet/brown solid (159 mg, 0.15 mmol, 80 %).

Found: C, 77.71; H, 5.63; N, 10.41. Calc. for C$_{68}$H$_{56}$N$_8$Cu: C, 77.87; H, 5.38; N, 10.68; λ_{max} (DCM)/nm 310 ($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1} 22), 349 (21), 408 (101), 444 (94), 525 (6.5), 563 (18), 601 (8.2); MS(MALDI/TOF) (MH$^+$) m/z found 1049.6. Calc. for C$_{68}$H$_{57}$N$_8$Cu 1049.8; EPR-parameters (THF, 77 K, simulated): $g_x = 2.053$, $g_y = 2.057$, $g_z = 2.190$, Cu: $A_x = 17$, $A_y = 20$, $A_z = 190$, N: $A_x = A_y = A_z = 15$.

CO$_2$ reduction experiments for Cu-1 and Cu-1-Ru

Cu-1 or **Cu-1-Ru** ($5 \cdot 10^{-4}$ mol/L) was dissolved in dry DMF (or acetonitrile) with 5 % dry triethylamine and this solution was purged with CO$_2$ for 20 minutes. This reaction mixture was illuminated with a LED-torch (stick-shaped printed board (19×1 cm) with 27 white LED’s (Nichia, type NSPW510DS, 400-800 nm) with a luminous efficiency of ca 10000 mcd per LED) for 20 hours in a schlenk tube with septum and the gas phase was subsequently analyzed by gas chromatography (Shimadzu GC-17A with TCD-detector and Carboxen®-1010 PLOT Capillary GC Column).

---

[1] T.A. Vanelli, T. B. Karpishin, *Inorg. Chem.*, 2000, **39(2)**, 340-347.

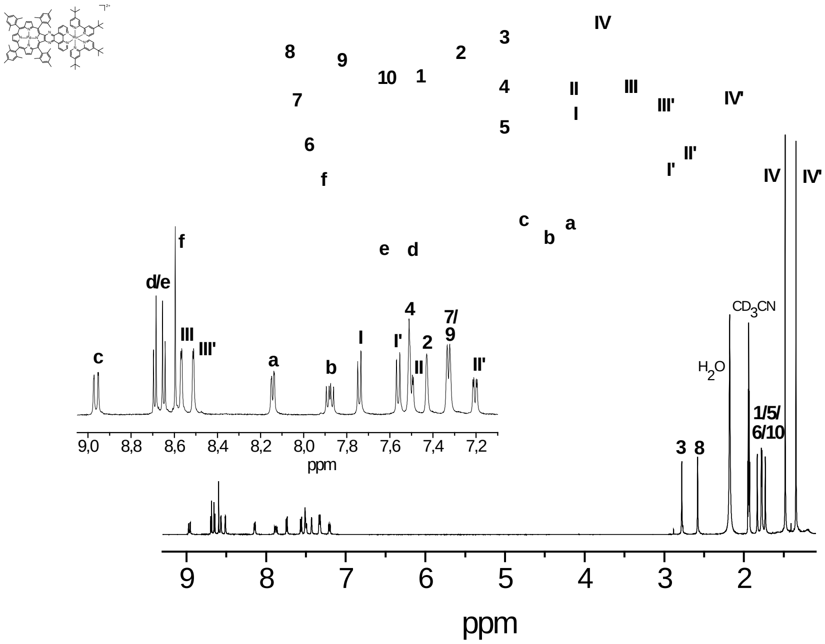

Figure S1: ^{1}H-NMR spectrum of **Pd-1-Ru** in CD_3CN.

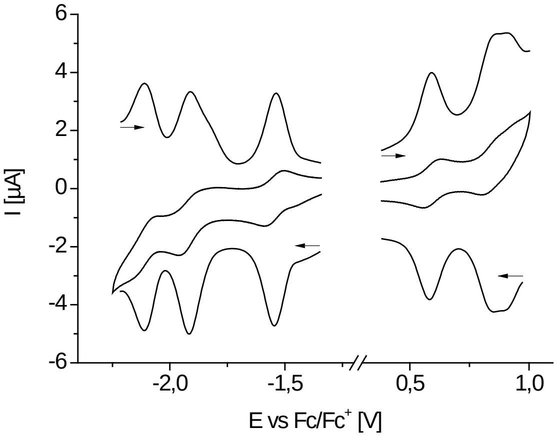

Figure S2: Cyclovoltammogram and square-wave-voltammogram of **Cu-1-Ru** in DCM containing 0.1 M TBAP.

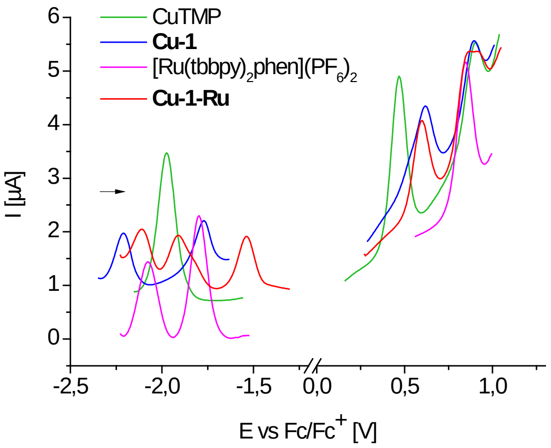

Figure S3: Square-wave-voltammograms of CuTMP, **Cu-1**, [Ru(tbbpy)$_2$phen](PF$_6$)$_2$ and **Cu-1-Ru** in DCM containing 0.1 M TBAP

For discussion see “electrochemistry”-chapter in main text.

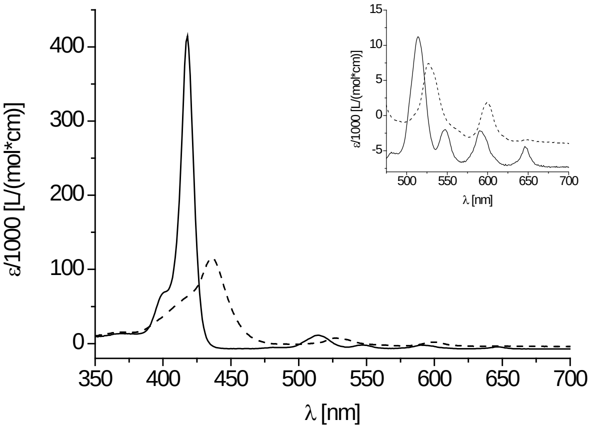

Figure S4: UV-Vis absorption spectra of H$_2$TMP (solid line) and **H$_2$-1** (dotted line) in DCM.

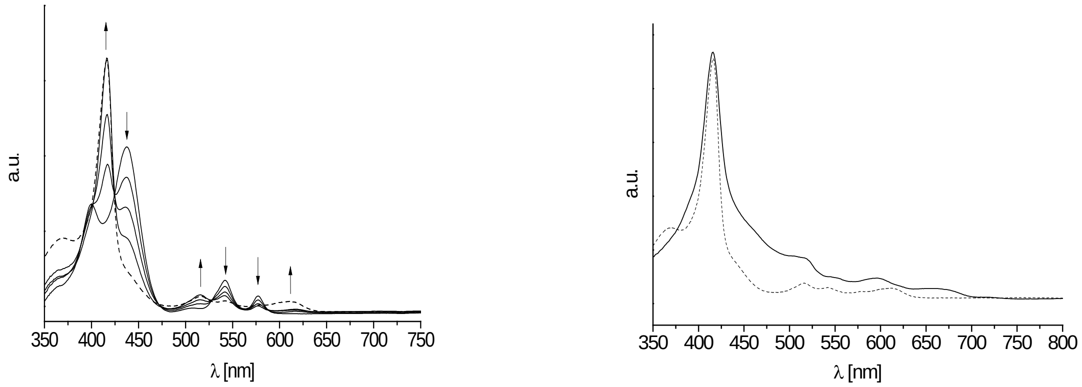

Figure S5: UV-Vis absorption spectral changes of a THF solution of **Pd-1** after illumination with LED light in the presence of 5 % TEA as sacrificial electron donor (left); UV-Vis absorption spectra in THF of: a) by Na(Hg) double-reduced **Pd-1** (solid line) and b) **Pd-1** after illumination (dotted line) (right)

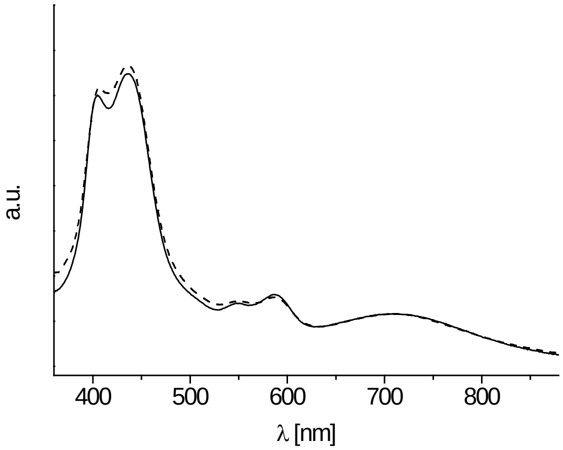

Figure S6: Overlay of UV-Vis-spectra of with NaHg mono-reduced **Cu-1-Ru** (solid line) and electrochemically mono-reduced **Cu-1-Ru** (dashed line) in ACN.