Synthesis and Photophysical and Electrochemical Study of Tyrosine Covalently Linked to High-Valent Copper(III) and Manganese(IV) Complexes

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As bio-inspired chemical model of the oxygen-evolving complex (OEC) in photosystem II, a new tyrosine-modified corrole ligand **3** and its high-valent copper and manganese complexes **3a** and **3b** were synthesized and characterized. The copper complexes **1a** and **2a** of corrole **1** and **2** were also prepared for comparison. The emission property indicates that the emission of ligands **2** and **3** is located at 670 nm, but no emission is observed for their metal complexes due to its suppression by the metal center. The electrochemical study shows that **3a** might dimerize at the first two reversible oxidations, a behavior which was not observed in the case of **1a** and **2a**. The corrolato manganese(IV) complex **3b** shows one reversible reduction and one quasireversible oxidation at −0.17 and 0.77 V *vs.* Ag/Ag$^+$, respectively.

Introduction. – The four-electron oxidation of water in photosynthetic organisms is achieved by an oxygen-evolving complex (OEC) in photosynthesis, which is one of the most important and fundamental chemical processes in nature [1–3]. A series of X-ray structure analysis of photosystem II (PS II) [4–6] indicated that the active site in a photosynthetic OEC protein contains a Mn_4Ca cluster [5][6], and a neighboring L-tyrosine (Tyr_z) is linked between P_{680} and OEC. By light absorption of the primary electron donor P_{680} consisting of chlorophyll *a* molecules, electron transfer occurs from the excited P_{680}* to a primary electron acceptor, pheophytin, and subsequently to two quinines, forming a P_{680} radical cation. The electrons produced by oxidation of water at the Mn_4Ca cluster are transferred through redox-active Tyr_z to $P_{680}^{+\bullet}$, which is reduced to P_{680} for another photosynthetic cycle. Tyr_z is crucial for the stabilization of the primary charge separation. Besides electron transfer, Tyr_z is thought to transfer its phenolic proton to a nearby base, leading to a neutral tyrosine radical [7–11]. Therefore, some tyrosine-containing metal complexes have been studied as artificial OEC models catalyzing water oxidation and simulating the process of proton-coupled electron transfer (PCET) [12–15]. As to the electron donor, oxidation of water at the Mn_4Ca cluster occurs in four steps and involves at least five oxidation states (S_0–S_4) [3][16]. Although the mechanism of O_2 evolution has not been determined completely, the stage of O_2 evolution would involve a high-valent manganese species [3][16–19].

Corroles are aromatic tetrapyrrole macrocycles, *i.e.*, ring-contracted analogues of porphyrins, which have proved to stabilize higher oxidation states of coordinated metals, comparable or superior to the more famous porphyrins, and many high-valent metal complexes have been synthesized and studied as catalysts and photosensitizers [20–26]. Therefore, we designed a ligand which contains a corrole and an L-tyrosine moiety connected through an amide bond, as well as its Mn-complex with the objective of studying water oxidation. In this paper, we report the synthesis and photophysical and electrochemical properties of the corrole ligand **3** and of its copper complex **3a** and manganese complex **3b**.

Results and Discussion. – *Synthesis and Characterization.* The synthesis of the L-tyrosine-containing corrole ligand **3** was accomplished in two steps from corrole **1**, which was obtained by the acid-catalyzed condensation reaction of 5-(4-methylphenyl)dipyrromethane and 3-nitrobenzaldehyde according to [27] (*Scheme*). After the reduction of the nitro group of **1** in the presence of $SnCl_2$ under acid conditions, **2** was obtained in 78% yield. The carboxy group of the *N*-Boc-protected L-tyrosine was then used to link to the amino group of **2**. Dicyclohexylcarbodiimide (DCC) was used as a dehydrating reagent and should be added after the mixture had been stirred at 0° for at least 0.5 h. All the reactions to synthesize **1**–**3** were performed under Ar and in the dark.

The preparation of [Cu^{III}(corrole)] and [Mn^{IV}(corrole)] complexes from $Cu(OAc)_2 \cdot H_2O$ and $Mn(OAc)_2 \cdot 4\,H_2O$, respectively, have been reported [25][28–33]. Similarly, the Cu complexes **1a**, **2a**, and **3a**, were obtained in high yield by reaction of corroles **1**–**3** with $Cu(OAc)_2 \cdot H_2O$ in pyridine at room temperature under air, decomposition being kept to a minimum. The Mn complex **3b** was obtained in 54% yield by reaction with $Mn(OAc)_2 \cdot 4\,H_2O$ in DMF under reflux under air.

The MS data of all compounds are given in the *Exper. Part*. The peak of the pseudomolecular ion $[\mathbf{3} + H]^+$ was observed at 833.4 in the API-ES-MS and at 833.3800 in the HR-ESI-MS, in agreement with the expected molecular formula. Well resolved ^1H-NMR spectra of **2** and **3** could not be obtained due to significant line broadening, which prevented a full assignment of the protons. In contrast, since a Cu^{III} complex was formed from **3**, the evident diamagnetism of **3a** made its ^1H-NMR spectrum well-resolved (*Fig. 1*). In addition, proton assignments for **3a** were also made based on peak intensity and multiplicity and verified by g-COSY. The two peaks located at δ 10.19 and 9.16 correspond to the phenol proton and the amide proton H–N(7)¹) of **3a**, respectively. The signal of the amide proton H–N(5)¹) adjacent to the carbonyl group at δ 4.26, coupled with the signal at δ 2.89 of a CH_2 group. The four broad peaks at δ 7.25, 7.35, 7.62, and 8.10 were attributed to the pyrrole protons. The signal around δ 7.62 integrated to six protons, *i.e.*, two pyrrole protons and four aromatic protons of the 4-methylphenyl moieties, the latter protons coupling with the other four protons of the 4-methylphenyl moieties at δ 7.39. The two protons of the CH_2 group are nonequivalent due to the chiral center C(4), thus giving rise to two *m* centered at δ 2.73 and 2.89. Only the proton of the latter signal coupled with the adjacent methine proton. The ^{t}Bu and the tolyl Me group appeared at δ 1.32 and 2.43, respectively. The MS, elemental

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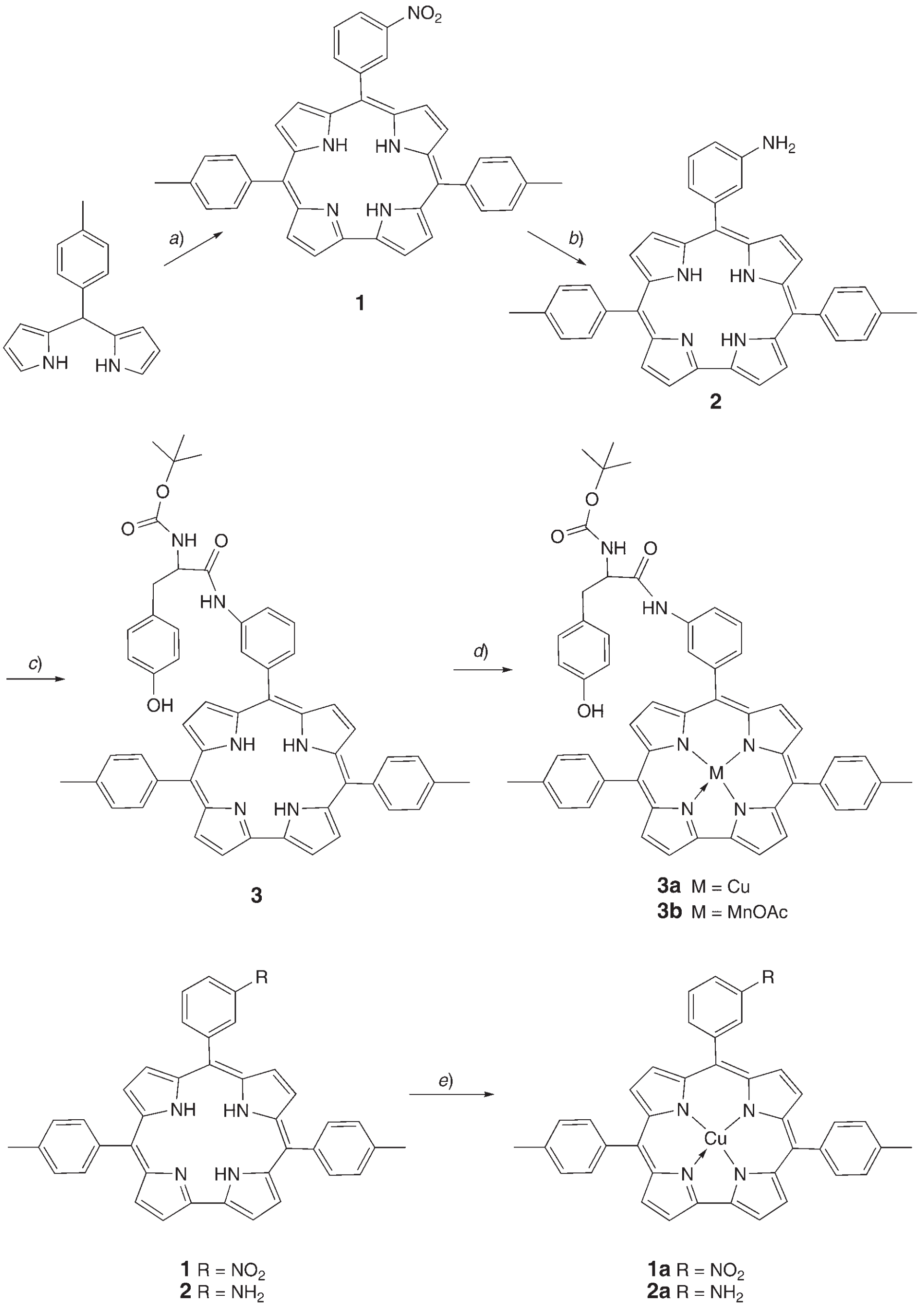
¹) Arbitrary atom numbering (*Fig. 1*); for systematic names, see *Exper. Part.*

Scheme. *Synthetic Route for Compounds* **3**, **3a**, **3b**, **1a**, *and* **2a**



a) 3-Nitrobenzaldehyde, CH_2Cl_2, CF_3COOH, r.t. 5 h; chloranil (=2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione), 2 h. *b*) $SnCl_2 \cdot 2\,H_2O$, $CHCl_3$/HCl/AcOH, 65°, 12 h. *c*) Boc-Tyr-OH, CH_2Cl_2, 0°, 0.5 h, DCC (=dicyclohexylcarbodiimide), r.t, 12 h. *d*) For **3a**, $Cu(OAc)_2 \cdot H_2O$, pyridine, r.t., 10 min; for **3b**, $Mn(OAc)_2 \cdot 4\,H_2O$, DMF, reflux, 10 min. *e*) $Cu(OAc)_2 \cdot H_2O$, pyridine, r.t., 10 min.

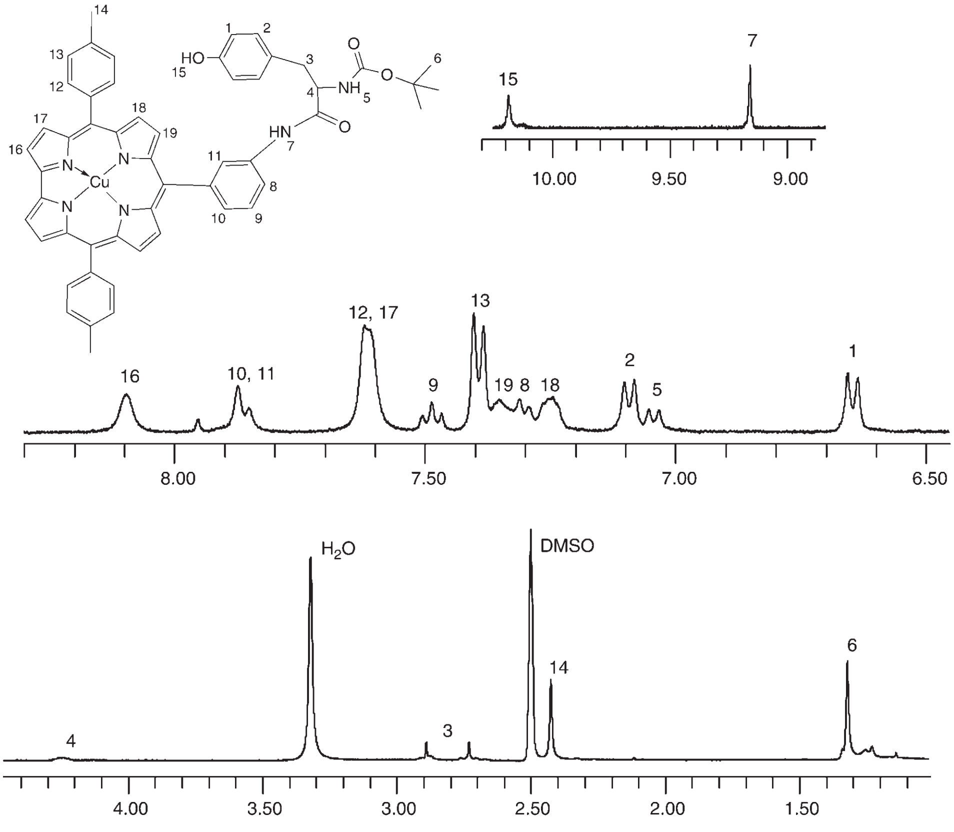


Fig. 1. *^{1}H-NMR Spectra of* **3a** *in (D_6)DMSO at 25°.* Arbitrary atom numbering.

analysis, and UV/VIS spectrum of **3a** not only confirmed the structure of the complex but also that of ligand **3**. Complex **3b** could not be characterized by ^{1}H-NMR as a result of its paramagnetic Mn-center, but the peaks at *m/z* 884.4 ($[M - \mathrm{OAc}]^+$) in the API-ES-MS and at 884.2894 in the HR-ESI-MS and the UV/VIS data confirmed its structure.

Absorption and Emission Spectra. The UV/VIS spectra of the free corrole ligand **3** and of the corresponding metal complexes **3a** and **3b** are shown in *Fig. 2*. The *Soret* band of **3** is located at 418 nm and that of the corrolatocopper **3a** at 417 nm. The Q-band of **3** displays three obvious absorptions at 577, 617, and 650 nm, respectively, while **3a** shows only one inconspicuous band at 539 nm. The compounds **1**, **1a**, **2**, and **2a** exhibit the same trend as **3** and **3a** (data, in the *Exper. Part*). Different from the corrolatocopper complexes, the *Soret* band of the Mn-complex **3b** is located at 437 nm, red-shifted by 22 nm in comparison to that of **3**. Besides this band, the UV/VIS spectrum of **3b** shows two other transitions at 317 and 367 nm and two poorly shaped bands at 518 and 607 nm in the Q-band, the spectrum exhibiting the typical pattern of [Mn^{IV}(corrolato)] complexes [32][33].

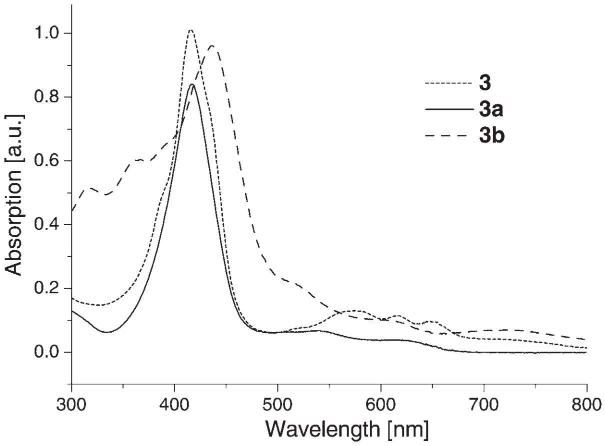


Fig. 2. *UV/VIS Spectra of* **3**, **3a**, *and* **3b** *in* CH_2Cl_2

The excitation and emission spectra of **3** and **2** were measured in CH_2Cl_2 at room temperature (*Fig. 3*). There are two bands in the excitation spectrum of **3** and **2**, with almost the same maximal wavelength at 414 and 567 nm (566 nm for **2**), belonging to the *Soret* and Q-band, respectively. When exciting the *Soret* band (414 nm) and Q-band (567 nm), the emission for both **3** and **2** is located at 670 nm. But the emission intensity upon irradiation at the *Soret* band is higher than that produced upon irradiation of the Q-band for both **3** and **2**, they correspond to the excitation intensity. The same emission wavelength of **3** and **2** means that the tyrosine moiety has little effect on the energy of S_0 and S_1 states of the corrol moiety. No emission was observed for **2a**, **3a**, and **3b** due to the suppression by the metal center.

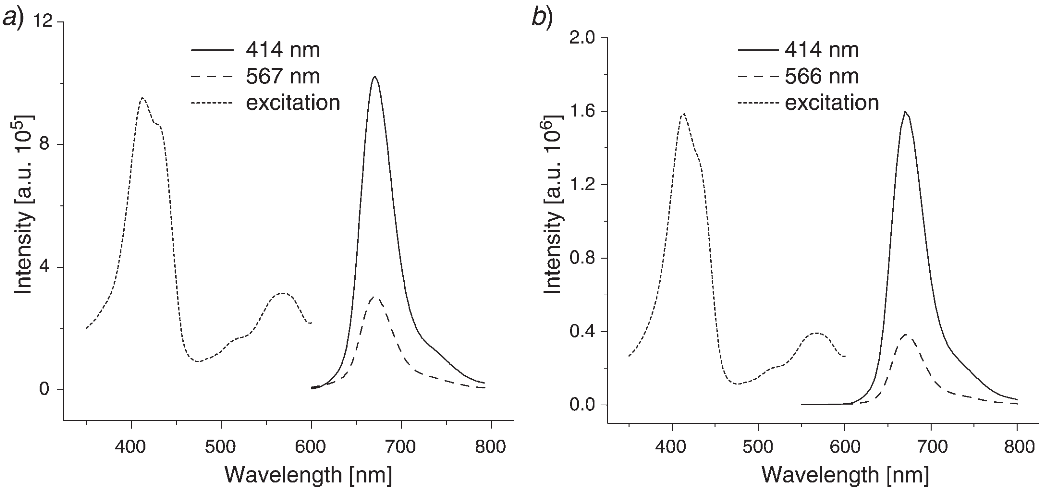


Fig. 3. *Room-temperature emission and excitation spectrum of* a) **3** *and* b) **2** *in* CH_2Cl_2

Electrochemistry Study. The cyclic voltammetry for the corrolatometal complexes **1a**, **2a**, **3a**, and **3b** (*Fig. 4*) was examined in CH_2Cl_2 containing 0.1M $(Bu_4N)PF_6$. Complex **1a** undergoes two reversible reductions at $E_{1/2} = -1.45$ and -0.46 V *vs.* Ag/Ag$^+$, which can be confidently assigned to the reduction of the nitro group and the metal center Cu^{III}/Cu^{II}, respectively, based on a comparison with nonmetal complexes of **1**. There are also two reversible oxidations at $E_{1/2} = 0.54$ and 1.28 V *vs.* Ag/Ag$^+$. The oxidation at $E_{1/2} = 0.54$ V can be assigned to the oxidation of the corrole ring. Compound **2a** undergoes a single reversible reduction of Cu^{III}/Cu^{II} at $E_{1/2} = -0.36$ V. Except for the two oxidations at $E_{1/2} = 0.56$ V (oxidation of the corrole) and $E_{1/2} =$ 1.26 V, **2a** undergoes an irreversible oxidation at $E_{pa} = 1.10$ V, caused by the oxidation of the amine function.

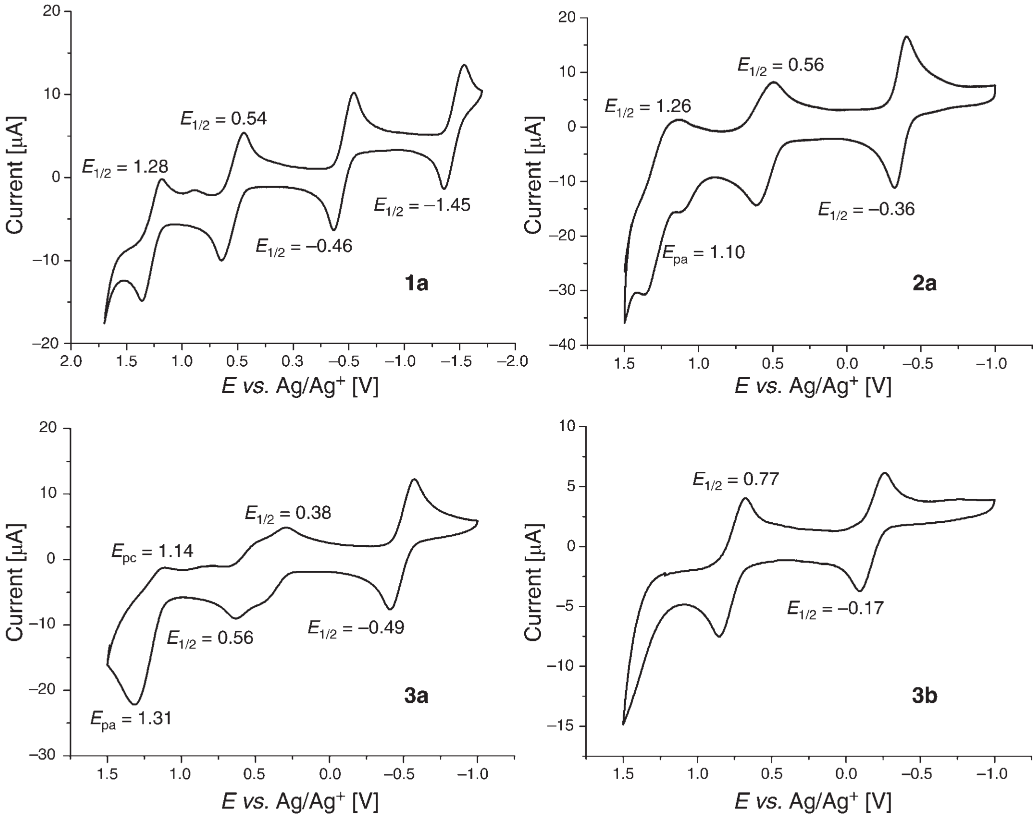


Fig. 4. *Cyclic voltammograms of* **1a**, **2a**, **3a**, *and* **3b** *in* CH_2Cl_2 $(Bu_4N)PF_6$ (0.1M) as supporting electrolyte, Ag/$AgNO_3$ as reference electrode, glass carbon disc electrode as working electrode; scan rate 0.1 V/s.

No evidence of dimerization is observed for **1a** and **2a** in both the first oxidation and the first reduction, which is different from the case of the well-known [Cu(oec)] (oec = 2,3,7,8,12,13,17,18-octaethylcorrolato(3–)) [34]. In the case of [Cu(oec)] the dimerization occurred upon oxidation, and the first two oxidations involved two stepwise abstractions of one electron from each macrocycle in the electrogenerated corrole $\pi-\pi$ dimer. It should be noted that also many triphenylcorrolato ligands show no evidence of dimerization [25][31]. This means that the bulky substituents at the corrole macrocycle must have a significant effect on the electrooxidation mechanism, and the phenyl substituents at the corrole macrocycle preclude the formation of dimers.

The electrochemical reduction of **3a** occurred at -0.49 V, which can be assigned to the reduction of Cu^{III}/Cu^{II}, while its electrochemical oxidation involves two reversible oxidations at $E_{1/2} = 0.38$ and 0.56 V and two irreversible oxidations at $E_{pc} = 1.14$ V and at $E_{pa} = 1.31$ V (broad peak). The [Mn(corrolato)] **3b** shows one reversible reduction and one quasireversible oxidation, with the $E_{1/2}$ values located at -0.17 and 0.77 V, respectively. Thus dimerization occurred in the case of **3a** in the oxidation, similarly to the behavior of [Cu(oec)], while no dimerization was found for the [Mn^{IV}(corrolato)] complex **3b**.

In contrast to what is seen for **3a**, no evidence of dimerization is observed for **1a**, **2a**, and many other triphenylcorrolatometals as mentioned above. This indicates that the L-tyrosine unit in **3a** must play a very important role in this dimerization reaction. The possible structure of the involved Cu^{III} dimer is currently under investigation.

Conclusions. – A novel L-tyrosine-modified corrole ligand and its copper(III) and mangane(IV) complexes were synthesized and characterized. The [Cu^{III}(Tyr-corrolato)] complex **3a** undergoes a series of multiple oxidations in CH_2Cl_2. The first two unusual reversible oxidations show that dimerization may occur, and only one electron from each macrocycle in the electrogenerated corrole $\pi-\pi$ dimer may be abstracted at each oxidation. One reversible reduction of the [Cu^{III}(Tyr-corrolato)] complex **3a** is also observed, this reduction involving the metal center.

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Experimental Part

General. All the reactions to synthesize **1**–**3** were conducted under Ar and in the dark. All solvents were dried and distilled prior to use according to the standard methods. Commercially available chemicals were used as received. The reagent Boc-L-Tyr-OH was purchased from *Aldrich Chemical Co.* CC = Column chromatography. ^{1}H-NMR Spectra: *Varian Inova-400* NMR spectrometer at 400 MHz and 298 K. MS: *HP 1100-MSD* instrument; *Micromass Q-TOF* micro spectrometer for high-resolution (HR); in *m*/*z*.

5,15-Bis(4-methylphenyl)-10-(3-nitrophenyl)corrole (**1**). To a soln. of 5-(4-methylphenyl)dipyrromethane (18.88 g, 80 mmol) and 3-nitrobenzaldehyde (6.08 g, 40 mmol) in CH_2Cl_2 (600 ml), CF_3COOH (30 µl, 0.39 mmol) was added, and the mixture was stirred at r.t. for 5 h. Then chloranil (19.68 g, 80 mmol) was added, and the mixture was stirred for another 2 h. The mixture was filtered through a short silica gel column (CH_2Cl_2), affording a mixture of **1** and several unidentified compounds. Subsequent CC (silica gel, CH_2Cl_2/hexanes 5 : 4) afforded pure **1** (2.10 g, 11%). Dark green solid. UV/VIS (CH_2Cl_2): 417, 580, 614, 655. ^{1}H-NMR ($CDCl_3$, 400 MHz): 2.68 (*s*, 2 *Me*C_6H_4); 7.63 (*d*, *J* = 7.2, 4 arom. H of MeC_6H_4); 7.92 (*t*, *J* = 7.2, 1 arom. H of $NO_2C_6H_4$); 8.23 (*d*, *J* = 6.4, 4 arom. H of MeC_6H_4); 8.41 (*s*, of Pyr 2 H); 8.48 (*d*, *J* = 7.2, 1 arom. H of $NO_2C_6H_4$); 8.58 (*s*, 1 arom. H of $NO_2C_6H_4$, 2 H of Pyr);

8.90 (*s*, 2 H of Pyr); 8.93 (*s*, 2 H of Pyr); 9.04 (*s*, 1 arom. H of $NO_2C_6H_4$). HR-ESI-MS (neg.): 598.2229 ($[M-H]^-$, $C_{39}H_{28}N_5O_2^-$; calc. 598.2243).

3-[5,15-Bis(4-methylphenyl)corrol-10-yl]benzenamine (**2**). $SnCl_2 \cdot 2\,H_2O$ (183 mg, 0.81 mmol) in 37% aq. HCl soln. (10 ml) was added to a soln. of **1** (120 mg, 0.2 mmol) in $CHCl_3$ (5 ml) and AcOH (10 ml). The resulting mixture was vigorously stirred under reflux (65–70°) overnight. After cooling to r.t., the pH of the mixture was brought to 8–9 with 25% NH_3 soln. $CHCl_3$ (50 ml) was added, the mixture stirred for 1 h, the aq. phase extracted with $CHCl_3$ (2 × 50 ml), the combined org. phase washed with 5% NH_3 soln. (1 ×) and H_2O (3 ×) and then concentrated, and the crude solid subjected to CC (silica gel, CH_2Cl_2/acetone 100:4): pure **2** (91 mg, 78%). Violet solid. UV/VIS (CH_2Cl_2): 417, 615. API-ES-MS: 1139.6 ($[2M+H]^+$), 570.3 ($[M+H]^+$). HR-ESI-MS: 570.2658 ($[M+H]^+$, $C_{39}H_{32}N_5^+$; calc. 570.2673).

N^1*-{3-[5,15-Bis(4-methylphenyl)corrol-10-yl]phenyl}-*N^2*-[(*tert*-butoxy)carbonyl]-*L*-tyrosinamide* (**3**). A soln. of **2** (57 mg, 0.1 mmol) and Boc-L-Tyr-OH (35 mg, 0.125 mmol) in CH_2Cl_2 (30 ml) was stirred at 0°. After 0.5 h, DCC (26 mg, 0.125 mmol) was added, and the mixture was left at r.t. for *ca.* 12 h. Then the mixture was concentrated and the residue subjected to CC (silica gel, CH_2Cl_2/acetone 1:1): **3** (79 mg, 95%). Violet solid. UV/VIS: 418, 577, 617, 650. API-ES-MS: 855.3 ($[M+Na]^+$), 833.4 ($[M+H])^+$. HR-ESI-MS: 833.3800 ($[M+1]^+$, $C_{53}H_{49}N_6O_4^+$; calc. 833.3815).

[5,15-Bis(4-methylphenyl)-10-(3-nitrophenyl)corrolato(3-)-$\kappa N^{21},\kappa N^{22},\kappa N^{23},\kappa N^{24}$*]copper* (**1a**). The soln. of **1** (60 mg, 0.1 mmol) and $Cu(OAc)_2 \cdot H_2O$ (60 mg, 0.3 mmol) in pyridine (10 ml) was stirred at r.t. for 5 min. The solvent was then evaporated and the crude solid purified by CC (silica gel, CH_2Cl_2/hexanes 1:2): **1a** (59 mg, 90%). Dark gray solid. UV/VIS (CH_2Cl_2): 417, 533. ^1H-NMR ($CDCl_3$, 400 MHz): 2.43 (*s*, 2 *Me*C_6H_4); 7.15 (*d*, *J* = 4.8, 2 H of Pyr); 7.31 (*d*, *J* = 7.6, 4 arom. H of MeC_6H_4); 7.38 (*d*, *J* = 4.8, 2 H of Pyr); 7.63 (*t*, *J* = 7.6, 1 arom. H of $NO_2C_6H_4$); 7.67 (*d*, *J* = 7.6, 4 arom. H of MeC_6H_4); 7.69 (*d*, *J* = 4.4, 2 H of Pyr); 7.90 (*d*, *J* = 4.0, 2 H of Pyr); 7.98 (*d*, *J* = 7.6, 1 arom. H of $NO_2C_6H_4$); 8.44 (*d*, *J* = 8.8, 1 arom. H of $NO_2C_6H_4$); 8.53 (*s*, 1 arom. H of $NO_2C_6H_4$). HR-ESI-MS (neg.): 659.1373 (M^-, $C_{39}H_{26}CuN_5O_2^-$; calc. 659.1382).

{3-[5,15-Bis(4-methylphenyl)corrol-10-yl-$\kappa N^{21},\kappa N^{22},\kappa N^{23};\kappa N^{24}$*]benzenaminato(3 –)}copper* (**2a**). As described for **1a** from **2** (57 mg, 0.1 mmol): **2a** (58 mg, 92%), after CC (silica gel, CH_2Cl_2/hexanes 1:1). UV/VIS (CH_2Cl_2): 415, 540. API-ES-MS: 625.5 ($[M+Na]^+$), 630.6 ($[M+H]^+$). ^1H-NMR ($CDCl_3$, 400 MHz): 2.44 (*s*, 2 *Me*C_6H_4); 3.77 (*s*, NH_2); 6.88 (*d*, *J* = 7.6, 1 arom. H of $NH_2C_6H_4$); 7.00 (*s*, 1 arom. H of $NH_2C_6H_4$); 7.08 (*d*, *J* = 8.0, 1 arom. H of $NH_2C_6H_4$); 7.23 (*t*, *J* = 7.6, 1 arom. H of $NH_2C_6H_4$); 7.30 (*d*, *J* = 7.6, 4 arom. H of MeC_6H_4); 7.35 (*s*, 4 H of Pyr); 7.68 (*d*, *J* = 7.6, 2 H of Pyr, 4 arom. H of MeC_6H_4); 7.88 (br. *s*, 2 H of Pyr). HR-ESI-MS: found 630.1728 ($[M+H]^+$, $C_{39}H_{29}CuN_5^+$; calc. 630.1719).

{N^1*-{3-[5,15-Bis(4-methylphenyl)corrol-10-yl-*$\kappa N^{21},\kappa N^{22},\kappa N^{23},\kappa N^{24}$*]phenyl}-*$N^2$*-(*tert*-butoxy)carbonyl]-*L*-tyrosinamidato(3–)}copper* (**3a**). As described for **1a**, from **3** (83 mg, 0.1 mmol): **3a** (67mg, 75%), after CC (silica gel, CH_2Cl_2/acetone 20:1). UV/VIS (CH_2Cl_2): 417, 539. ^1H-NMR (400 MHz, (D_6)DMSO, 25°)[1]): 1.32 (*s*, ^{t}Bu); 2.43 (*s*, 2 *Me*C_6H_4); 2.70–2.76 (*m*, 1 H, $CH_2(3)$); 2.86–2.92 (*m*, 1 H, $CH_2(3)$); 4.26 (br. *s*, H–C(4)); 6.64 (*d*, *J* = 8.4, 2 arom. H of Tyr); 7.05 (*d*, *J* = 8.0, 1 H, CONH); 7.09 (*d*, *J* = 8.4, 2 arom. H of Tyr); 7.25 (br. *s*, 2 H of Pyr); 7.30 (*d*, *J* = 7.6, 1 arom. H of NHC_6H_4); 7.35 (br. *s*, 2 H of Pyr); 7.39 (*d*, *J* = 7.6, 4 arom. H of MeC_6H_4); 7.49 (*t*, *J* = 7.6, 1 arom. H of NHC_6H_4); 7.62 (br. *s*, 2 H of Pyr, 4 arom. H of MeC_6H_4); 7.86 (*d*, *J* = 9.2, 2 arom. H of NHC_6H_4); 8.10 (br. *s*, 2 H of Pyr); 9.16 (*s*, N*H*C_6H_4); 10.19 (*s*, OH). API-ES-MS: 927 ($[M+Cl]^-$), 915.5 ($[M+Na]^+$), 892.3 (M^-). Anal. calc. for $C_{53}H_{45}CuN_6O_4 \cdot 0.5\,CH_2Cl_2$: C 68.65, H 4.95, N 8.98; found: C 68.97, H 5.04, N 9.38.

(Acetato-κO*){*N^1*-{3-[5,15-bis(4-methylphenyl)corrol-10-yl-*$\kappa N^{21};\kappa N^{22},\kappa N^{23},\kappa N^{24}$*]phenyl}-*$N^2$*-(*tert*-butoxy)carbonyl]-*L*-tyrosinamidato(3–)}manganese* (**3b**). A soln. of **3** (83 mg, 0.1 mmol) and an excess of manganese(II) acetate tetrahydrate (0.25 g, 1.0 mmol) in DMF (10 ml) was refluxed under air for 10 min. After the solvent was evaporated, the residue was subjected to CC (silica gel, CH_2Cl_2/acetone 10:1): pure **3b** (48 mg, 54%). Brown solid. UV/VIS (CH_2Cl_2):317, 367, 437, 721. API-ES-MS: 884.4 ($[M-OAc]^+$). HR-ESI-MS 884.2894 ($[M-OAc]^+$), $C_{53}H_{45}MnN_6O_4^+$; calc. 884.2883).

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