ChemPubSoc Europe

DOI: 10.1002/ejic.201600714

EurJIC European Journal of Inorganic Chemistry

Full Paper

Porphrinoids

Siamese-Twin Porphyrins: Variation of Two *meso*-Aryl Groups

Oliver Mitevski,[a] Sebastian Dechert,[a] Christian Brückner*[b] and Franc Meyer*[a]

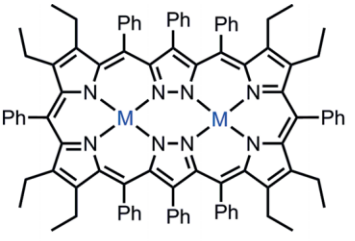
Abstract: Variation of two out of the six *meso*-aryl groups in Siamese-twin porphyrin, an expanded porphyrin incorporating two pyrazole moieties, identified a set of substituents that result in optimized preparation of highly crystalline products. Electron-donating and electron-withdrawing aryl substituents have only negligible electronic and structural influences on the free-base macrocycles (as measured by their UV/Vis absorption spectra and solid-state structures, respectively) and their dicopper complexes (as measured by their cyclic voltammograms).

Introduction

Expanded porphyrins (i.e., porphyrinoids containing more than 18 aromatic π-electrons or more than four heterocyclic building blocks) are much investigated. This is because of their NIR absorption, their ability to coordinate simultaneously to two metal ions, and their conformational flexibility affecting macrocycle π-conjugation and aromaticity.[1]

We contributed to this field by introducing Siamese-twin porphyrin (STP) **1a**, thus named because of its two fused porphyrin-like binding pockets that are linked through pyrazole moieties.[2] This nonplanar and non-macrocycle-aromatic molecule is characterized by the presence of two binding pockets whose N_4 coordination mean planes are nearly orthogonal to each other. We were able to prepare a number of homo- and heterodimetallic complexes, such as **1aCu$_2$** and **1aNiCu**.[2,3] We also demonstrated the electronic interaction between the metal centers and the enormous influence of the central metal atoms on the electronic properties of the macrocycle. Except for a description of the oxidation chemistry of free base **1a**,[4] we have not reported on any structural variations of parent STP **1a**.

All peripheral positions of the macrocycle are substituted by either ethyl groups (pyrrole β-positions) or phenyl groups (*meso* positions and 4-position of the pyrazole). The choice of the substituents and the particular substituent pattern was guided by practical synthesis considerations (i.e., the symmetric 3,4-diethylpyrrole is readily accessible[5] and does not give rise to the formation of regioisomers) and to induce the proper conformation of the precursor Siamese-twin porphyrinogen to allow its oxidation to the final product **1a**. We also found that the *meso*-phenyl groups adjacent to the pyrazole groups were necessary for the oxidation of this position to take place; left unsubstituted, these positions resisted oxidation.[2,6]



1a, M = 2H
1aCu$_2$, M = Cu
1aNiCu, M = Ni, Cu
1aNi$_2$, M = Ni

A variation of some (or all) of the *meso* groups perceivably modulates the electronic properties of the STP macrocycle, even though the *meso*-phenyl groups are (in the solid state) in an idealized orthogonal arrangement to the mean plane of the portion of the macrocycle to which they are attached.[2] However, in analogy to the findings in *meso*-arylporphyrins, some rotational freedom of the *meso*-phenyl groups can be assumed, with the transition state of the rotation possibly being stabilized by resonance effects.[7] Moreover, inductive effects of the *meso*-phenyl substituents are operative. Even though the electronic effects of various *meso*-aryl substituents are small, they are not negligible.[8] *meso*-Alkylporphyrins are also electronically much distinct from their *meso*-aryl congeners.[9]

We describe herein the results of a systematic variation of the two *meso*-aryl groups in STPs that are located between pyrrolic subunits along the long axis of the macrocycle and their effects on the yield of the reaction, the crystallinity of the products, and their electronic and structural effects.

Results and Discussion

Synthesis of Free-Base *meso*-Aryl STPs

Of all the substituents on the STP framework, in principle, none are as readily varied as the *meso*-phenyl group located between

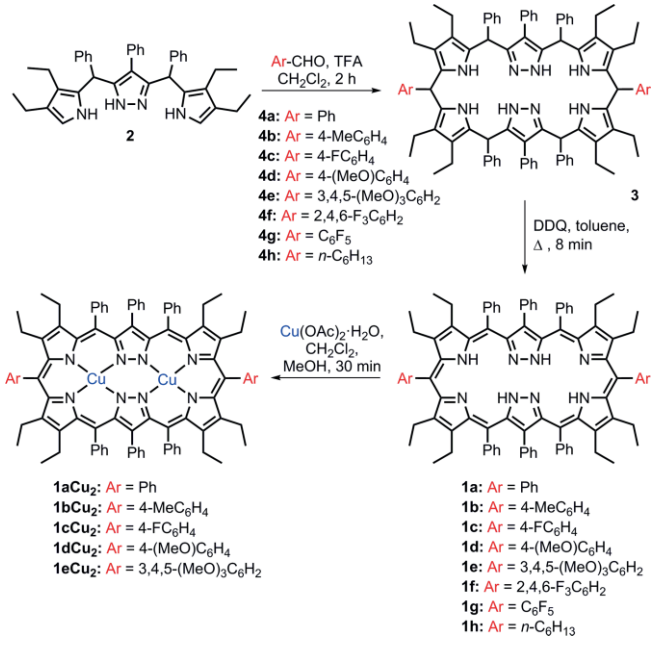
[a] *Institute of Inorganic Chemistry, Georg-August-University, Tammannstrasse 4, 37077 Göttingen, Germany*
E-mail: franc.meyer@chemie.uni-goettingen.de
http://www.meyer.chemie.uni-goettingen.de
[b] *Department of Chemistry, Unit 3060, University of Connecticut, Storrs, CT 06269-3060, USA*
E-mail: c.bruckner@uconn.edu
http://bruckner.research.uconn.edu
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejic.201600714.

Table 1. Experimental findings and Hammett parameters of the arenecarbaldehydes used.

Aldehyde	Yield of **1** [%][a]	$\Sigma\sigma$[b]	λ_{max} [nm][c]
a: PhCHO	50[d] (23)[e]	0 (by definition)	640
b: 4-MeC_6H_4CHO	24	–0.17	640
c: 4-FC_6H_4CHO	9	0.06	637
d: 4-$(MeO)C_6H_4CHO$	27	–0.27	640
e: 3,4,5-$(MeO)_3C_6H_2CHO$	15	–0.03	640
f: 2,4,6-$F_3C_6H_2CHO$	–[f]	0.06	–
g: C_6F_5CHO	–[f]	0.74	–
h: *n*-$C_6H_{13}CHO$	n.d.[g]	–	–

[a] Isolated yield of (micro)crystalline material based on dipyrrolylpyrazole **2** used in the synthesis. [b] Sum of the Hammett parameters of a single *meso*-aryl group, as per ref.[10] [c] Longest wavelength of absorption (in CH_2Cl_2); see also Figure 1. [d] Ref.[2] [e] The high yield reported in ref.[2] could not be reproduced on a routine basis at the larger scales reported here. [f] Detected by MS; no material isolated. [g] Not detected.

two pyrrolic moieties (Scheme 1).[2,3b] All it requires is the variation of the arenecarbaldehyde in the 3+3 condensation step of dipyrrolylpyrazole **2** with an arenecarbaldehyde to produce porphyrinogen **3**. This intermediate is subsequently oxidized to the final product **1**. Its practical realization, however, proved to be more problematic.



Scheme 1. Synthesis of STPs **1a**–**1h** and the corresponding copper complexes **1aCu$_2$**–**1eCu$_2$**.

We used a series of arenecarbaldehydes containing electron-donating and electron-withdrawing substituents and heptanal for the cyclization of **2** according to the standard literature procedure for the preparation of **1a**.[2,3b] All of the aldehydes tested resulted in the formation of the corresponding porphyrinogen **3**, which was isolated as a mixture of multiple stereoisomers by column chromatography on basic aluminum oxide and immediately oxidized with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The yields of isolated STP derivatives **1** are listed in Table 1. The STP derivatives were spectroscopically characterized and showed all the expected analytical data (see also Supporting Information). On a routine basis, we observed the singly and doubly protonated $[M + H]^+$and $[M + 2 H]^{2+}$ species in the ESI+ mass spectra, another indication for the distinct electronic independence of each pyrrolic binding pocket in the STPs shown previously also in solution-state investigations.[2]

The widely varying yields of the isolated products are noteworthy. They vary from traces for **1g** to 9 % for **1c** to satisfactory yields of 24 and 27 % for **1b** and **1d**, respectively. While we expected aldehydes carrying strongly electron-withdrawing substituents [e.g., 2,4,6-trifluoro- and 2,3,4,5,6-pentafluorobenzaldehydes (**4f** and **4g**)] to be more susceptible to nucleophilic attack and thus react faster than the electron-rich aldehydes, this did not translate into higher yields of the final product. This effect may be due to a decreased reactivity of the porphyrinogen precursor in the oxidation step. Thus, we find the use of *meso*-C_6F_5 groups not to have any benefits, even though this *meso* substituent has been particularly popular in the field of corroles and expanded macrocycles.[11] Conversely, the somewhat more electron-rich aldehydes **4b** and **4d** produced high yields of product. Heptanal (**4h**) led to the formation of an unstable product that could not be characterized as an STP (by HRMS and UV/Vis spectroscopy). Thus, *p*-tolualdehyde (**4b**), 4-fluorobenzaldehyde (**4c**), 4-methoxybenzaldehyde (**4d**), and 3,4,5-trimethoxybenzaldehyde (**4e**) allowed the synthesis of the corresponding STPs in multi-100 mg batches (from 2 g of **2** in 350 mL of solvent). The degrees of crystallinity of the substituted STPs also differ significantly, and contribute to the higher yields for some of the products. In addition, the substituents modulate to a noticeable degree the solubility of the STPs. In particular, the presence of methoxy groups much increased the solubility of the SPTs in polar solvents such as acetone and methanol.

UV/Vis Spectra of Free-Base *meso*-Aryl STPs

The UV/Vis spectra of the STPs **1b**–**1e** (Figure 1) are all as expected, and nearly identical to the spectrum of all-phenyl derivative **1a**. The differences observed in their extinction coefficients are within the error of the measurement.

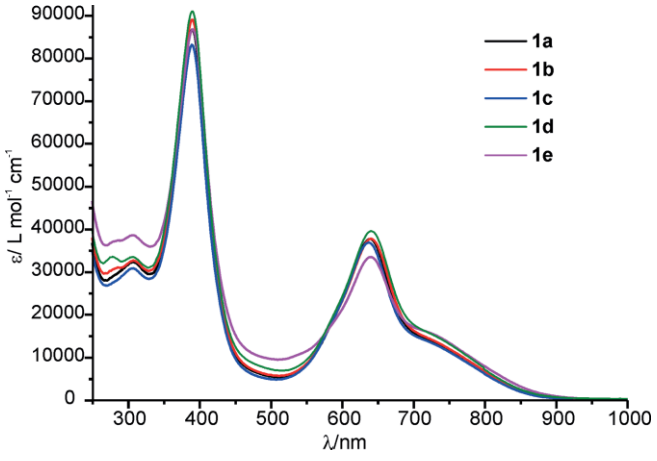


Figure 1. UV/Vis spectra (CH_2Cl_2) of STPs **1**.

Solid-State Structures of Free-Base *meso*-Aryl STPs 1b and 1c

We determined the single-crystal X-ray structures of **1c** (Figure 2) and **1b** (not shown, see Supporting Information). The framework structures of **1a**, **1b**, and **1c** are all nearly identical to each other, although the compounds crystallized in different space groups (**1a**: $P\bar{1}$;[4] **1b**,**1c**: $P2_1/c$). Thus, changing two of the *meso* substituents did not alter the twisted conformation of the macrocycle (Figure 3). This underlines the conformational rigidity of the macrocycle imposed by the substituents, which was previously also shown experimentally.[3]

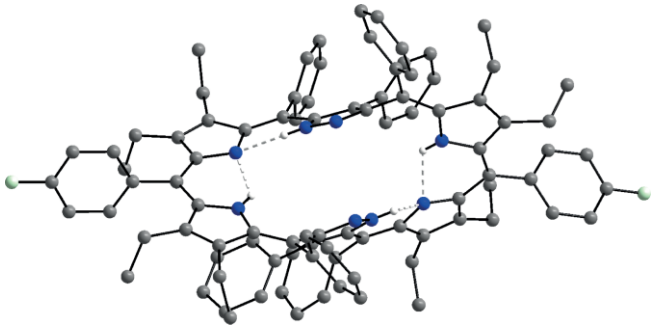


Figure 2. Ball-and-stick model of the molecular structure of **1c**, determined by single-crystal XRD. All carbon-bound hydrogen atoms, disorder, and solvent molecules are omitted for clarity (gray: carbon; blue: nitrogen; green: fluorine; white: hydrogen). For details, see Supporting Information.

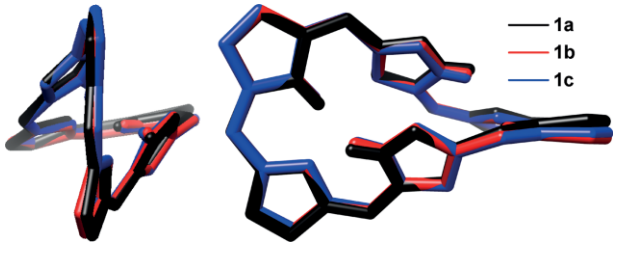


Figure 3. Overlay of the macrocycle core structures of **1a** (black),[4] **1b** (red), and **1c** (blue), as determined by single-crystal XRD, indicating their near-identical conformations. For details, see Supporting Information.

DFT calculations were shown to predict the conformations of STPs and their metal complexes with high fidelity.[2,3] The computed conformations of **1d** and **1e** indicated retention of the conformation observed and calculated for **1a**, that is, the perpendicular arrangement of the aryl groups also prevents any steric clashes between the aryl substituents and the neighboring β-ethyl groups (see Supporting Information).

Formation of the Dicopper Complexes $1Cu_2$ of the *meso*-Aryl STPs

The blue dicopper complexes **1bCu$_2$**–**1eCu$_2$** were formed by reaction of the free-base STPs with a source of copper(II) in a polar solvent (Scheme 1), as described previously for the formation of **1aCu$_2$**,[2,3] but by using a modified purification protocol. All dicopper complexes showed the expected analytical data. Mirroring the trend seen for the free bases, the UV/Vis spectra of the dicopper complexes were also nearly identical (see Supporting Information).

Cyclic Voltammetry of the Dicopper Complexes $1Cu_2$

The STP dicopper complex **1aCu$_2$** exhibited well-defined redox waves in its cyclic voltammogram, associated with oxidations that mainly take place at the dipyrromethene subunits of the macrocycle.[3a] It thus could be expected that the oxidation potentials of the copper complexes **1bCu$_2$**–**1eCu$_2$** would reflect the electronic influence of the *meso*-aryl groups. This is indeed the case (Figure 4, Table 2).

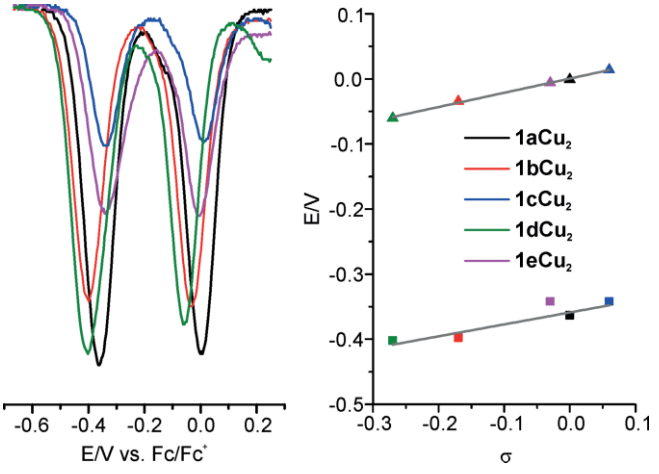


Figure 4. Left: Square-wave voltammograms of **1aCu$_2$**–**1eCu$_2$** (CH_2Cl_2, 0.1 M $[Bu_4N]PF_6$). Right: Hammett plots of the first (lower line) and second (upper line) oxidation potentials of **1aCu$_2$**–**1eCu$_2$** vs. Fc/Fc^+; the data for **1eCu$_2$** were excluded from the linear regression of the first oxidation potentials.

Cyclic (see Supporting Information) and square-wave voltammetry measurements of the dicopper complexes **1aCu$_2$**–**1eCu$_2$** showed the expected two oxidation events.[3a,3c] The potentials are shifted to higher values with the electron-withdrawing fluorine substituent and to lower values with electron-donating substituents, and the shifts conform to a linear Hammett corre-

Table 2. Potential difference of the first two oxidations of the different metal complexes in comparison to **1aCu$_2$**[a] and the corresponding *meso*-tetrakis(aryl)porphyrin complexes.

Complex	ΔE(Ox1)	ΔE(Ox2)	Ref.
1aCu$_2$	0 mV[b]	0 mV[b]	[3a]
1bCu$_2$	–35 mV	–34 mV	this work
1cCu$_2$	20 mV	14 mV	this work
1dCu$_2$	–40 mV	–60 mV	this work
1eCu$_2$	20 mV	–6 mV	this work
1aCuNi	30 mV	260 mV	[3c]
1aNi$_2$	210 mV	320 mV	[3c]
TPPCu[c]	0 mV[b]	0 mV[b]	[12a]
T(*p*Me)PPCu[d]	–70 mV	–20 mV	[8d]
T(*p*OMe)PPCu[e]	–140 mV	–	[12b]
TPPNi[f]	10 mV	60 mV	[12c]

[a] Values as determined by square-wave voltammetry (in CH_2Cl_2, 0.1 M $[Bu_4N]PF_6$), cf. Figure 4. [b] By definition. [c] (*meso*-tetraphenylporphyrinato)copper(II). [d] [*meso*-tetrakis(4-methyphenyl)porphyrinato]copper(II). [e] [*meso*-tetrakis(4-methoxyphenyl)porphyrinato]copper(II). [f] (*meso*-tetraphenylporphyrinato)nickel(II).

lation (Figure 4 and Supporting Information). Only the first oxidation peak of the trimethoxyphenyl-substituted complex **1eCu$_2$** lies outside this trend (see Supporting Information for more details).

The exchange of one or both copper ions with one or two nickel ions has a much bigger influence on the corresponding redox potentials than the substitution patterns of the two *meso*-aryl groups (Table 2). In comparison, the shifts observed in the corresponding *meso*-tetraarylporphyrin copper complexes **T(*p*-X)PPCu**[8d,12a,12b] on variation of the (four) *meso*-aryl groups are significantly larger, while the shifts on switching the metal from copper to nickel are much smaller than those observed for the STP complexes. This further underlines the fundamentally different electronic structures of the non-macrocycle-aromatic STPs compared to the aromatic porphyrins.

Conclusions

We synthesized a number of free-base and dicopper STPs in which the two *meso*-aryl groups flanked by two pyrrole moieties were varied with differently strong electron-donating or electron-withdrawing substituents. The influence of this variation on the experimental and computed structures of the STP core is vanishingly small. Likewise, the influence on the electronic structure of the free-base macrocycles and their dicopper complexes, as assessed by their nearly identical optical spectra, is minute. On the other hand, the oxidation potentials of the dicopper complexes are somewhat more affected by the substituents, which reflects their influence on the oxidation site, namely, the dipyrromethene subunits of the STP that include the *meso* position to which the substituents are attached.

Such derivatization is thus unsuitable to significantly modulate the electronic structure of STPs. However, their influence on the synthetic yield, solubility, and degree of crystallinity of the STPs are remarkably large. Particularly the *meso*-tetraphenylbis(tolyl) derivative **1b** is suitable for further investigation of the chemistry of the STPs owing to its ease of synthesis on relatively large scales, solubility, relative chemical stability, and crystallinity.

Experimental Section

Materials: STP **1a** was synthesized according to a literature procedure.[2,4] All other materials were obtained from commercial suppliers and used as received.

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer at 238 K. Chemical shifts δ are reported in ppm relative to residual proton and carbon signals of CD_2Cl_2 at δ = 5.32 ppm and 54.00 ppm, respectively. HRMS measurements were recorded with a Bruker Maxis ESI-QTOF-MS spectrometer by using MeOH as a carrier solvent. UV/Vis spectra were recorded with a Varian Cary 5000 spectrophotometer using quartz cuvettes. IR spectra were recorded with a Bruker VERTEX 70 spectrometer.

Computation: DFT calculations were carried out with the ORCA program (version 3.0.3).[13] Atom coordinates were obtained from the crystal structure of the parent STP[4] and refined by using the Becke–Perdew 1986 functional (BP86) and the def2-tzvp basis set for the copper atoms and the def2-svp basis set for all other atoms.[3a] Structure optimizations of all compounds readily converged.

Crystal Structure Analysis: XRD data for **1b** and **1c** were collected with a STOE IPDS II diffractometer (graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å) by use of ω-scans at –140 °C (Table S1). For further details, see Supporting Information. CCDC 1484865 (for **1b**) and 1484866 (for **1c**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Cyclic Voltammetry: Electrochemical measurements were performed in dichloromethane with $[Bu_4N]PF_6$ (0.1 M) as electrolyte by using a Perkin–Elmer 263A potentiostat controlled by Electrochemistry Powersuite software (Princeton Applied Research). A glassy-carbon electrode was used as working electrode, together with a platinum wire counter electrode and a silver reference electrode. Decamethylferrocene was added as internal standard ($E_{1/2}$ = 0.59 V vs. Fc/Fc^+).[14]

General Procedure for the Synthesis of STPs 1b–1e: Aldehydes **4b**–**4e** (0.180 mmol) and 3,5-bis(3,4-diethyl-1*H*-pyrrol-2-ylbenzyl)-1*H*-pyrazole (**2**; 0.180 mmol, 100 mg, 1.0 equiv.) were dissolved in dichloromethane (18.6 mL) and protected from light. TFA (180 µL, 1 M in CH_2Cl_2, 0.180 mmol, 1.0 equiv.) was added, and the solution was stirred for 2 h. The solvent was reduced to less than 5 % of its volume, and the solution was filtered through a plug of basic aluminum oxide. The only fraction that passed through was the porphyrinogen, which was obtained as a yellow solid after removal of the solvent (approximate yields of **1b**: 66 mg, 27 %; **1c**: 65 mg, 27 %; **1d**: 45 mg, 18 %; **1e**: 46 mg, 17 %). Typically, it was directly used in the subsequent oxidation step, but if needed can be stored under nitrogen in the freezer. Porphyrinogens **3b**–**3e** (0.310 mmol) were dissolved in toluene (60.0 mL) at 80 °C, and DDQ (1.24 mmol, 280 mg, 4.0 equiv.) was added all at once, and the solution was stirred at 80 °C for 8 min. The solvent was then immediately removed under reduced pressure. The residue was dissolved in *tert*-butyl methyl ether/CH_2Cl_2/EtOAc (10:3:1) and filtered through a plug of basic aluminum oxide. The only fraction that passed through the column was raw product **1**. These crude fractions were further purified by column chromatography (silica; MeOH). STPs **1b**–**1e** were obtained as bluish green solids.

1b: Yield of isolated product: 99 mg (24 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 238 K): δ = 13.36 (s, 1 H, NH^{pz}), 11.32 (s, 1 H, NH^{pyr}), 7.54 (m, 2 H, Ph), 7.23–7.34 (m, 5 H, Ph), 6.97 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.84 [d, ^3J(H-H) = 7.7 Hz, 1 H, Ph], 6.92 [d, ^3J(H-H) = 7.7 Hz, 1 H, Ph],6.79 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.74 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.55 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.29 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.17 [d, ^3J(H-H) = 7.7 Hz, 1 H, Ph], 2.32 (s, 3 H, CH_3),1.98 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2],1.86 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2],1.55 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2],1.55 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2], 1.43 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2],1.20 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.20 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2],0.89 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.55 [t, ^3J(H-H) = 7.3 Hz, 6 H, CH_3], 0.45 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3],0.41 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3] ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 238 K): δ = 167.7 (Ph), 151.4 (Ph), 151.2 (Ph),148.2 (Ph),147.5 (Ph),145.3 (Ph),141.4 (Ph),141.3 (Ph),140.7 (Ph),139.4 (Ph),139.1 (Ph), 137.4 (Ph),135.3 (Ph),134.8 (Ph),133.9 (Ph),133.1 (Ph),132.9 (Ph),132.5 (Ph),132.3 (Ph),131.6 (Ph),130.7 (Ph),128.3 (Ph),127.9 (Ph),127.8 (Ph),127.7 (Ph),127.7 (Ph),127.6 (Ph),127.2 (Ph),127.2 (Ph),127.0 (Ph),126.5 (Ph),126.5 (Ph),126.1 (Ph),124.4 (Ph),124.2 (Ph),123.9 (Ph),113.8 (Ph),106.0 (Ph),21.4 (CH_3),18.9 (CH_2),18.5 (CH_2),18.1 (CH_2),18.0 (CH_2),16.3 (CH_3),15.9 (CH_3),15.6 (CH_3),14.7 (CH_3) ppm. IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε [L mol^{-1} cm^{-1}]) = 278 (30600), 307 (32700), 390 (89000), 640 (37800), 734 (13500) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1329.7217 (calcd. 1329.7205) [M + H]$^+$, 665.3634 (calcd. 665.3639) [M + 2 H]$^{2+}$.

1c: Yield of isolated product: 37 mg (9 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 238 K): δ = 13.34 (s, 1 H, NH^{pz}), 11.37 (s, 1 H, NH^{pyr}), 7.48–7.55 (m, 2 H, Ph), 7.21–7.38 (m, 5 H, Ph), 7.13–7.17 (m, 1 H, Ph), 6.89–7.05 (m, 5 H, Ph), 6.83–6.86 (m, 1 H, Ph),6.79 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.75 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.56 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph],6.29 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.17 [d, ^3J(H-H) = 7.7 Hz, 1 H, Ph], 1.98 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2],1.86 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2],1.57 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2], 1.45 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2],1.20 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.90 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.56 [t, ^3J(H-H) = 7.3 Hz, 6 H, CH_3], 0.45 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3],0.42 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3] ppm ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 238 K): δ = 167.5 (Ph), 163.5 (Ph), 161.5 (Ph), 151.4 (Ph), 151.2 (Ph), 148.4 (Ph), 147.8 (Ph), 145.0 (Ph), 141.8 (Ph), 141.1 (Ph), 140.4 (Ph), 139.3 (Ph), 139.1 (Ph), 135.2 (Ph), 134.7 [d, ^3J(C-F) = 7.9 Hz, *p*-F-C_6H_4], 134.2 [d, ^3J(C-F) = 7.9 Hz, *p*-F-C_6H_4], 134.1 (Ph), 134.1 (Ph), 133.8 (Ph),133.1 (Ph), 132.3 (Ph),131.6 [d, ^1J(C-F) = 227.7 Hz, *p*-F-C_6H_4], 131.6 (Ph), 128.0 (Ph), 127.8 (Ph), 127.7 (Ph), 127.3 (Ph), 127.2 (Ph), 127.1 (Ph), 126.6 (Ph), 126.5 (Ph), 126.2 (Ph), 124.4 (Ph), 124.0 (Ph), 114.6 [d, ^2J(C-F) = 21.0 Hz, *p*-F-C_6H_4], 114.4 (Ph), 114.1 [d, ^2J(C-F) = 21.0 Hz, *p*-F-C_6H_4], 104.6 (Ph), 18.9 (CH_2), 18.5 (CH_2), 18.2 (CH_2), 18.1 (CH_2), 16.2 (CH_3), 15.9 (CH_3), 15.5 (CH_3), 14.8 (CH_3) ppm. ^{19}F NMR (470 MHz, CD_2Cl_2, 238 K): δ = 115.3 (m) ppm. IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 306 (30877), 389 (83182), 637 (36908), 734 (12717 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1337.6704 (calcd. 1337.6703) [M + H]$^+$, 669.3384 (calcd. 669.3388) [M + 2 H]$^{2+}$.

1d: Yield of isolated product: 113 mg (27 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 238 K): δ = 13.37 (s, 1 H, NH^{pz}), 11.33 (s, 1 H, NH^{pyr}), 7.49–7.55 (m, 2 H, Ph), 7.21–7.37 (m, 5 H, Ph), 7.06 [dd, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 7.02 [dd, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.97 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.93 [dd, ^4J(H-H) = 2.0, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.84 [dd, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.79 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.69–6.76 (m, 3 H, Ph), 6.55 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.29 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.17 [dd, ^3J(H-H) = 7.7 Hz, 1 H, Ph], 3.76 (s, 3 H, OCH_3), 1.98 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.87 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.56 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2], 1.44 [q, ^3J(H-H) = 7.3 Hz, 2 H, CH_2], 1.24 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.94 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.56 [t, ^3J(H-H) = 7.3 Hz, 6 H, CH_3], 0.45 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3], 0.43 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3] ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 238 K): δ = 167.8 (Ph), 159 (Ph), 151.4 (Ph), 151.2 (Ph), 148.4 (Ph), 147.5 (Ph), 145.3 (Ph), 141.4 (Ph), 141.3 (Ph), 140.7 (Ph), 139.4 (Ph), 139.1 (Ph), 135.3 (Ph), 134.1 (Ph), 133.9 (Ph), 133.5 (Ph), 133.1 (Ph), 132.4 (Ph), 132.4 (Ph), 131.6 (Ph), 130.7 (Ph), 130.1 (Ph), 127.9 (Ph), 127.7 (Ph), 127.7 (Ph), 127.2 (Ph), 127.2 (Ph), 127.0 (Ph), 126.5 (Ph), 126.5 (Ph), 126.1 (Ph), 124.4 (Ph), 124.2 (Ph), 123.9 (Ph), 113.9 (Ph), 112.5 (Ph), 112.4 (Ph), 105.5 (Ph), 55.3 (OCH_3), 18.9 (CH_2), 18.5 (CH_2), 18.2 (CH_2), 18.1 (CH_2), 16.3 (CH_3), 16.0 (CH_3), 15.6 (CH_3), 14.8 (CH_3) ppm. IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 277 (33500), 306 (33600), 390 (91000), 640 (39600), 734 (14700 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1361.7104 (calcd. 1361.7103) [M + H]$^+$, 681.3582 (calcd. 681.3588) [M + 2 H]$^{2+}$.

1e: Yield of isolated product: 67 mg (15 %). ^{1}H NMR (500 MHz, CD_2Cl_2, 238 K): δ = 13.20 (s, 1 H, NH^{pz}), 11.49 (s, 1 H, NH^{pyr}), 7.48–7.54 (m, 2 H, Ph), 7.21–7.35 (m, 5 H, Ph), 7.00 [dd, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.96 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.83 [dd, ^4J(H-H) = 1.5, ^3J(H-H) = 7.7 Hz, 1 H, Ph], 6.78 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.72 [td, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.54 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.43 [d, ^4J(H-H) = 1.5, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.31 [td, ^4J(H-H) = 1.3, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 6.21 [d, ^4J(H-H) = 1.5 Hz, 1 H, Ph], 6.13 [dd, ^4J(H-H) = 2.0, ^3J(H-H) = 7.5 Hz, 1 H, Ph], 3.79 (s, 3 H, OCH_3), 3.71 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 2.01 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.90 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.63 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.56 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.38–1.45 (m, 2 H, CH_2), 1.30 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 1.10 [q, ^3J(H-H) = 7.3 Hz, 1 H, CH_2], 0.65 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3], 0.56 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3], 0.52 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3], 0.44 [t, ^3J(H-H) = 7.3 Hz, 3 H, CH_3] ppm. ^{13}C NMR (125 MHz, CD_2Cl_2, 238 K): δ = 167.1 (Ph), 152.3 (Ph), 151.7 (Ph), 151.4 (Ph), 151.1 (Ph), 148.4 (Ph), 147.8 (Ph), 145.3 (Ph), 141.7 (Ph), 141.2 (Ph), 140.7 (Ph), 139.5 (Ph), 139.1 (Ph), 137.1 (Ph), 135.3 (Ph), 134.1 (Ph), 133.7 (Ph), 133.2 (Ph), 132.6 (Ph), 132.5 (Ph), 131.7 (Ph), 130.8 (Ph), 127.9 (Ph), 127.8 (Ph), 127.7 (Ph), 127.7 (Ph), 127.3 (Ph), 127.2 (Ph), 127.0 (Ph), 126.6 (Ph), 126.4 (Ph), 126.1 (Ph), 123.9 (Ph), 114.8 (Ph), 109.6 (Ph), 108.8 (Ph), 105.9 (Ph), 60.9 (OCH_3), 55.9 (OCH_3), 55.7 (OCH_3), 18.9 (CH_2), 18.5 (CH_2), 18.1 (2 C, CH_2), 16.7 (CH_3), 16.0 (CH_3), 15.9 (CH_3), 14.7 (CH_3) ppm. IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 278 (37200), 306 (38700), 390 (86800), 640 (33500), 734 (15000 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1481.7526 (calcd. 1481.7526) [M + H]$^+$, 741.3794 (calcd. 741.3799) [M + 2 H]$^{2+}$.

1f: HRMS (ESI$^+$, MeOH): *m/z* (%) = 1409.6327 (calcd. 1409.6326) [M + H]$^+$, 705.3198 (calcd. 705.3200) [M + 2 H]$^{2+}$.

1g: HRMS (ESI$^+$, MeOH): *m/z* (%) = 1481.5955 (calcd. 1481.5950) [M + H]$^+$, 741.3005 (calcd. 741.3011) [M + 2 H]$^{2+}$.

General Procedure for the Synthesis of STP Dicopper Complexes $\mathbf{1bCu_2}$–$\mathbf{1eCu_2}$: $Cu(OAc)_2{\cdot}H_2O$ (69.0 mg, 345.6 μmol, 9.0 equiv.) was added to a solution of **1b**–**1e** (38.4 μmol, 1.0 equiv.) in dichloromethane (10 mL) and methanol (20 mL) and the reaction mixture stirred at ambient temperature for 30 min. The solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and filtered through a plug of basic aluminum oxide. The filtrate contained the desired product; removal of the solvent yielded the copper complexes $\mathbf{1Cu_2}$ as blue solids.

$\mathbf{1bCu_2}$: Yield of isolated product: 33.6 mg (60 %). IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 284 (31700), 391

(55900), 578 (13400), 636 (24000), 682 (18200 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1450.5394 (calcd. 1450.5405) $[M]^+$.

1cCu$_2$: Yield of isolated product: 10.3 mg (18 %). IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 300 (30700), 390 (59100), 549 (14400), 632 (25400), 682 (19200 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1458.4890 (calcd. 1458.4904) $[M]^+$.

1dCu$_2$: Yield of isolated product: 29.4 mg (52 %). IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 291 (34200), 389 (58500), 542 (21500), 639 (21900), 682 (19200 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1482.5295 (calcd. 1482.5304) $[M]^+$.

1eCu$_2$: Yield of isolated product: 41.1 mg (67 %). IR (KBr): see Supporting Information. UV/Vis (CH_2Cl_2): λ_{max} (ε) = 300 (31300), 389 (57100), 546 (20000), 632 (21000), 682 (18000 L mol^{-1} cm^{-1}) nm. HRMS (ESI$^+$, MeOH): *m/z* (%) = 1602.5720 (calcd. 1602.5726) $[M]^+$.

Acknowledgments

This work was supported by the Georg-August-University Göttingen (to F. M.) and the US National Science Foundation, grant CHE-1465133 (to C. B.).

Keywords: Porphyrinoids · Expanded porphyrins · Copper · Electronic structure · Cyclic voltammetry

[1] a) R. Misra, T. K. Chandrashekar, *Acc. Chem. Res.* **2008**, *41*, 265–279; b) M. Stępień, L. Latos-Grażyński, *Top. Heterocycl. Chem.* **2009**, *19*, 83–153; c) S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2011**, *50*, 4342–4373; *Angew. Chem.* **2011**, *123*, 4432; d) Y. Pareek, M. Ravikanth, T. K. Chandrashekar, *Acc. Chem. Res.* **2012**, *45*, 1801–1816; e) S. Shimizu, N. Aratani, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 4909–4918.

[2] L. K. Frensch, K. Pröpper, M. John, S. Demeshko, C. Brückner, F. Meyer, *Angew. Chem. Int. Ed.* **2011**, *50*, 1420–1424; *Angew. Chem.* **2011**, *123*, 1456.

[3] a) L. K. Blusch, K. E. Craigo, V. Martin-Diaconescu, A. B. McQuarters, E. Bill, S. Dechert, S. DeBeer, N. Lehnert, F. Meyer, *J. Am. Chem. Soc.* **2013**, *135*, 13892–13899; b) L. K. Blusch, Y. Hemberger, K. Pröpper, B. Dittrich, F. Witterauf, M. John, G. Bringmann, C. Brückner, F. Meyer, *Chem. Eur. J.* **2013**, *19*, 5868–5880; c) L. K. Blusch, O. Mitevski, V. Martin-Diaconescu, K. Pröpper, S. DeBeer, S. Dechert, F. Meyer, *Inorg. Chem.* **2014**, *53*, 7876–7885.

[4] A. Vogel, S. Dechert, M. John, C. Brückner, F. Meyer, *Chem. Eur. J.* **2016**, *22*, 2307–2316.

[5] J. L. Sessler, A. Mozaffari, M. R. Johnson, *Org. Synth.* **1992**, *70*, 68–78.

[6] S. Katsiaouni, S. Dechert, R. P. Briñas, C. Brückner, F. Meyer, *Chem. Eur. J.* **2008**, *14*, 4823–4835.

[7] a) S. S. Eaton, G. R. Eaton, *J. Am. Chem. Soc.* **1975**, *97*, 3660–3666; b) S. S. Eaton, G. R. Eaton, *J. Am. Chem. Soc.* **1977**, *99*, 6594–6599; c) Y. Okuno, T. Kamikado, S. Yokoyama, S. Mashiko, *THEOCHEM* **2002**, *594*, 55–60.

[8] a) J. S. Lindsey in *The Porphyrin Handbook*, vol. 1 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 45–118; b) P. J. Spellane, M. Gouterman, A. Antipas, S. Kim, Y. C. Liu, *Inorg. Chem.* **1980**, *19*, 386–391; c) P. G. Gassman, A. Ghosh, J. Almlöf, *J. Am. Chem. Soc.* **1992**, *114*, 9990–10000; d) G. Hariprasad, S. Dahal, B. G. Maiya, *J. Chem. Soc., Dalton Trans.* **1996**, 3429–3436; e) J. Kim, J. J. Leonard, F. R. Longo, *J. Am. Chem. Soc.* **1972**, *94*, 3986–3992.

[9] R. Plamont, Y. Kikkawa, M. Takahashi, M. Kanesato, M. Giorgi, A. Chan Kam Shun, C. Roussel, T. S. Balaban, *Chem. Eur. J.* **2013**, *19*, 11293–11300.

[10] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165–195.

[11] a) W.-Y. Cha, T. Soya, T. Tanaka, H. Mori, Y. Hong, S. Lee, K. H. Park, A. Osuka, D. Kim, *Chem. Commun.* **2016**, *52*, 6076–6078; b) M. Ishida, S.-J. Kim, C. Preihs, K. Ohkubo, J. M. Lim, B. S. Lee, J. S. Park, V. M. Lynch, V. V. Roznyatovskiy, T. Sarma, P. K. Panda, C.-H. Lee, S. Fukuzumi, D. Kim, J. L. Sessler, *Nature Chem.* **2012**, *5*, 15–20; c) J.-Y. Shin, H. Furuta, A. Osuka, *Angew. Chem. Int. Ed.* **2001**, *40*, 619–621; *Angew. Chem.* **2001**, *113*, 639; d) J. Pellegrino, S. E. Bari, D. E. Bikiel, F. Doctorovich, *J. Am. Chem. Soc.* **2010**, *132*, 989–995; e) A. Srinivasan, T. Ishizuka, A. Osuka, H. Furuta, *J. Am. Chem. Soc.* **2003**, *125*, 878–879; f) J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.* **2001**, *123*, 7190–7191; g) S. Saito, K. Furukawa, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 2128–2129; for the importance of C_6F_5 groups for the reactivity in porphyrins, see: h) B. Hu, J. Li, *Angew. Chem. Int. Ed.* **2015**, *54*, 10579–10582; *Angew. Chem.* **2015**, *127*, 10725; i) Y. Han, H. Fang, H. Jing, H. Sun, H. Lei, W. Lai, R. Cao, *Angew. Chem. Int. Ed.* **2016**, *55*, 5457–5462; *Angew. Chem.* **2016**, *128*, 5547–5552.

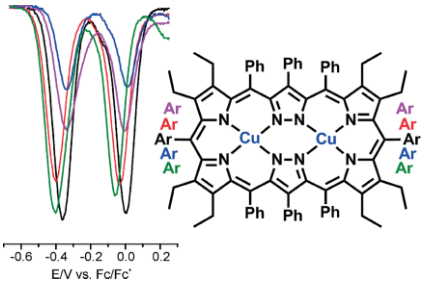
[12] a) K. M. Kadish, M. M. Morrison, *Bioinorg. Chem.* **1977**, *7*, 107–115; b) A. Wolberg, *Isr. J. Chem.* **1974**, *12*, 1031–1035; c) D. Chang, T. Malinski, A. Ulman, K. M. Kadish, *Inorg. Chem.* **1984**, *23*, 817–824; for the shift of the redox potentials in **T(*p*-X)PPNi** complexes, see: K. M. Kadish, M. Lin, E. Van Caemelbecke, G. De Stefano, C. J. Medforth, D. J. Nurco, N. Y. Nelson, B. Krattinger, C. M. Muzzi, L. Jaquinod, Y. Xu, D. C. Shyr, K. M. Smith, J. A. Shelnutt, *Inorg. Chem.* **2002**, *41*, 6673–6687; for a collection of redox potentials, see: K. M. Kadish, G. Royal, E. van Caemelbecke, L. Gueletti, *The Porphyrin Handbook*, vol. 9 (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 1–220.

[13] F. Neese, *ORCA*, Max Planck Institute for Chemical Energy Conversion, Mühlheim/Ruhr, Germany, **2012**.

[14] N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.

Received: June 14, 2016
Published Online: ■

Porphrinoids



The electronic and structural effects of the variation of two of the peripheral *meso*-aryl groups of Siamese-twin porphyrins are small to negligible, but because of solubility and crystallinity modulations, the new derivatives have multiple benefits.

DOI: 10.1002/ejic.201600714