Fang, Y.; Senge, M. O., Van Caemelbecke, E.; Smith, K. M.; Medforth, C. J.; Zhang, M.; Kadish, K. M. (2014):
Impact of Substituents and Nonplanarity on Nickel and Copper Porphyrin Electrochemistry: First Observation of a CuII/CuIII Reaction in Nonaqueous Media.
Inorganic Chemistry **53**, 10772–10778.

Impact of Substituents and Nonplanarity on Nickel and Copper Porphyrin Electrochemistry – First Observation of a Cu(II)/Cu(III) Reaction in Nonaqueous Media

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ABSTRACT Electrochemical studies of the oxidation of dodecasubstitued and highly nonplanar nickel porphyrins in a non-coordinating solvent have previously revealed the first Ni^{III} porphyrin dication. Herein, we investigate if these nonplanar porphyrins can also be used to detect the so far unobserved Cu^{III} porphyrin dication. Electrochemical studies of the oxidation of (DPP)M and (OETPP)M show three processes, the first two of which are macrocycle centered to give the porphyrin dication followed by a $Cu^{II/III}$ processes at more positive potential. Support for the assignment of the $Cu^{II/III}$ process comes from the linear relationships observed between $E_{1/2}$ and the third ionization potential of the central metal ions for Fe, Co, Ni and Cu complexes of (DPP)M and (OETPP)M. In addition, the oxidation behaviour of additional nonplanar nickel porphyrins is investigated in a non-coordinating solvent, with nickel *meso*-tetraalkylporphyrins also being found to form Ni^{III} porphyrin dications. Finally, examination of the nickel *meso*-tetraalkylporphyrins in a coordinating solvent (pyridine) reveals that the first oxidation becomes metal-centered under these conditions, as previously noted for a range of nominally planar porphyrins.

INTRODUCTION

Numerous transition metal porphyrins containing iron, cobalt, nickel or copper central metal ions have been investigated over the last fifty years as to their electrochemical properties under a variety of solution conditions.[1,2] Studies of "simple" metalloporphyrins containing substituted TPP (5,10,15,20-tetraphenylporphyrin) or OEP (2,3,7,8,12,13,17,18-octaethylporphyrin) macrocycles led to a fairly good understanding of the expected redox potentials, separations between redox processes and sites of electron transfer as a function of porphyrin structure, metal oxidation state, number and type of bound axial ligands and specific solvent/supporting electrolyte system.[3]

Simple electrochemical criteria were formulated and utilized many times to suggest the site of electron transfer during studies in the 1960s, 1970s and 1980s.[3] For example, in the case of OEP complexes, the absolute potential difference between the first porphyrin ring-centered oxidation yielding a π-cation radical and the first porphyrin ring-centered reduction yielding a π-anion radical (the HOMO-LUMO gap) was said to be 2.25 ± 0.15 V independent of the central metal ion oxidation state,[4,5] the only exception being derivatives of Mo and Mn.[4,5] A similar HOMO-LUMO gap was seen for TPP complexes.[6] The expected potential difference between the first and second ring oxidations of octaethylporphyrins or tetraphenylporphyrins was generally 0.29 ± 0.05 V while that between the first and second ring reductions was often 0.42 ± 0.05 V.[6] These three potential differences were then used as key diagnostic criteria for assigning the site of electron transfer in early studies of OEP and TPP-type derivatives[3] and the same criteria continue to be used today in many publications reporting the electrochemistry of metalloporphyrins in nonaqueous media.

However, in the 1990s, a large number of non-planar porphyrins containing copper, iron, cobalt or nickel central metal ions were synthesized by Smith and coworkers,[7-17] and the electrochemical properties of these compounds were then investigated in nonaqueous media.[12-15,18,19] These electrochemical studies showed that previously utilized electrochemical diagnostic criteria for assigning the sites of electron transfer might no longer be applicable. For example, the potential separation between the two ring-centered oxidations of many non-planar Ni^{II} porphyrins was often equal to zero in CH_2Cl_2 containing 0.1 M TBAP as supporting electrolyte, i.e., the two one-electron oxidations were overlapped to give an overall two electron transfer process in a single step.[3,12]

The number of redox processes a transition metal porphyrin will undergo, as well as the site of oxidation and reduction in these compounds, will often vary with the solution conditions used to carry out the electrochemical measurements. For example, in solvents such as CH_2Cl_2, PhCN or THF, most cobalt(II) porphyrins can be oxidized in three successive one-electron transfer steps, the first of which unambiguously involves a Co^{II}/Co^{III} redox process.[3,20] However, (TPP)Co and related cobalt(II) porphyrins can also undergo a ring-centered redox process in the first electron abstraction. In coordinating solvents or solvents containing trace water, the first electron is abstracted from the Co^{II} center[3,20] but an initial oxidation at the porphyrin π-ring system was shown to occur for (TPP)Co in a very dry dichloromethane solvent,[21] and this was followed by a $Co^{II/III}$ process, either in the second or third of the three observed oxidation processes.

Such changes in the site of electron transfer for oxidation of $(TPP)Ni^{II}$ and other Ni^{II} porphyrins may also be accomplished by changes in the solvent. For example, the

first oxidation is metal-centered in pyridine[22,23] and macrocycle-centered in non-bonding or weakly coordinating solvents such as CH_2Cl_2 or PhCN.[3] The potentials for the first two oxidations of (TPP)Ni^{II} are very close to each other in some solvent/supporting electrolyte systems[6] and the site of the first electron transfer can be easily shifted from the conjugated π-ring system to the metal or from the metal to the π-system by changes in temperature,[24] phenyl ring substituents,[25] and/or the planarity of the macrocycle.[12,22]

A third oxidation to give the Ni^{III} dication was expected to occur after formation of the Ni^{II} dication radical in non-coordinating solvents but no more than two oxidation processes were ever reported for any Ni^{II} porphyrin until 1993, when it was shown that three successive one-electron oxidations were exhibited by Ni^{II} derivatives containing a non-planar macrocycle such as OMTPP (2,3,7,8,12,13,1,7,18-octamethyl-5,10,15,20-tetraphenylporphyrin) or OETPP (2,3,7,8,12,13,1,7,18-octaethyl-5,10,15,20-tetraphenylporphyrin),[18] the third of which involves the $Ni^{II/III}$ process at relatively positive potentials. In a detailed electrochemical study of different Ni^{II} porphyrins,[12] the potential separation between the first two, ring-centered, oxidations was shown to vary between 0.0 and 400 mV depending upon a variety of factors, including the nonplanarity of the macrocycle, the type of π-cation radical, a_{1u} vs. a_{2u}, and the ability of anions from the supporting electrolyte to complex to the oxidized species.

The principal goal of the present work is to probe the limits of nonplanar porphyrins in facilitating the detection of $M^{II/III}$ processes and investigate the possibility of observing a Cu(II)/Cu(III) porphyrin dication redox process, which is expected to occur at more positive potentials than even the Ni(II)/Ni(III) couple. The Cu(II)/Cu(III) process has never been experimentally observed but should occur in porphyrins as it does

in the structurely related corroles, which exist in a stable Cu(III) oxidation state.[26-34] Using the nonplanar copper(II) porphyrins, (DPP)Cu[9] and (OETPP)Cu,[7] we show that nonplanar porphyrin macrocycles can be oxidized in three one-electron transfer steps, the last of which does indeed involve formation of a Cu(III) porphyrin dication at extremely positive potentials.

The paper is divided into three Sections. Sections 1 and 2 describe studies of the electrochemistry in non-coordinating or coordinating solvents, respectively, of a series of nickel tetraalkyporphyrins (see Chart 1) with varying degrees of nonplanarity. The studies reported in Section 1 were required because formation of the Ni^{III} porphyrin dication has only been reported for a handful of very nonplanar porphyrins and it was important to confirm that this process can be observed for other easily oxidizable and nonplanar Ni^{II} porphyrins. In Section II, the effect of a coordinating solvent on the oxidation processes of nonplanar nickel porphyrins is examined for the first time. It is demonstrated that nonplanar nickel porphyrins in coordinating solvents show a switch to oxidation at the metal centre for the first oxidation, as noted previously for nominally planar porphyrins. Having confirmed the presence of the Ni^{III} dication for a range of other nickel porphyrins, and clarified the effect of coordinating solvents on the Ni(II)/Ni(III) oxidation, Section 3 describes investigations of the Cu(II)/Cu(III) redox processes in (DPP)Cu and (OETPP)Cu.

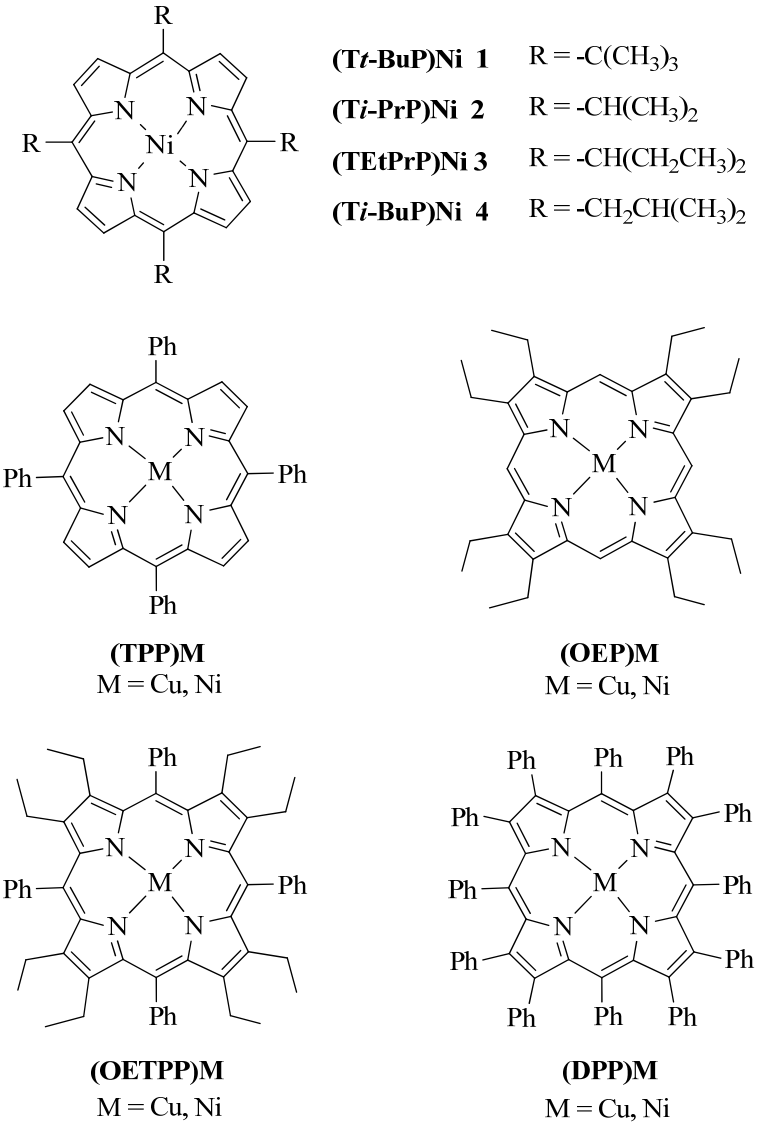

Chart 1. Structures of the investigated porphyrins.

EXPERIMENTAL SECTION

Chemicals. Benzonitrile (PhCN), obtained from Fluka Chemika or Aldrich Co., was distilled over phosphorous pentoxide (P_2O_5) under vacuum prior to use. Absolute dichloromethane (CH_2Cl_2) and pyridine were received from Aldrich Co. and used as received. High purity N_2 from Trigas was used to deoxygenate the solution before each

electrochemical experiment. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Fluka Chemika Co. and used without further purification.

(DPP)Ni,[9] (DPP)Cu,[9] (OETPP)Ni[7], (OETPP)Cu[7] and the tetraalkyl nickel(II) porphyrins[35,36] were synthesized as described in the literature.

Instrumentation. Cyclic voltammetry (CV) measurements were performed at 298 K on an EG&G model 173 potentiostat coupled with an EG&G model 175 universal programmer in deaerated PhCN solution containing 0.1 M TBAP as a supporting electrolyte. A three-electrode system composed of a glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE) was utilized. The reference electrode was separated from the bulk of the solution by a fritted-glass bridge filled with the solvent/supporting electrolyte mixture.

RESULTS AND DISCUSSION

I. Electrochemistry of Nonplanar Nickel Tetraalkylporphyrins in Non-Coordinating Solvents. Cyclic voltammograms of the four investigated Ni^{II} tetraalkylporphyrins, (T*t*-BuP)Ni **1**, (T*i*-PrP)Ni **2**, (TEtPrP)Ni **3** and (T*i*-BuP)Ni **4,** are shown in Figure 1. In the solid state, these porphyrins adopt progressively more nonplanar structures as the *meso* substituents become bulkier when changing from primary alkyl groups (**4**) to secondary alkyl groups (**3** and **2**) and finally to tertiary alkyl groups (**1**).[35]

Compounds **1**, **2** and **3** undergo two one-electron reductions and three one-electron oxidations within the potential range of the solvent (+2.0 to -2.0 V vs SCE). Compound **4** undergoes three oxidations, and one reduction, with the second reduction not being observed in PhCN. The first reduction of all four compounds occurs at similar

$E_{1/2}$ values of -1.44 to -1.46 V vs SCE as seen in Figure 1. The first oxidation of the porphyrins with less bulky primary or secondary alkane substituents (T*i*-PrP)Ni **2**, (TEtPrP)Ni **3** and (T*i*-BuP)Ni **4** are also similar to each other ($E_{1/2}$ = 0.89 to 0.92 V). This is not the case for the second oxidation of these three derivatives which follows the order of **4** (1.06 V) < **3** (1.10 V) < **2** (1.18 V). Compound **1** is the most distorted of the four investigated tetraalkylporphyrins and the first two oxidations are shifted negatively as compared to the reactions of compounds **2**, **3** and **4** (by 160-190 mV for the first oxidation and 110-230 mV for the second oxidation). The third (metal-centered) oxidation of compounds **1**-**4** also varies significantly as a function of the peripheral substituents, with $E_{1/2}$ values ranging from 1.82 for **4** to 1.58 V for **1** (see Table 1).

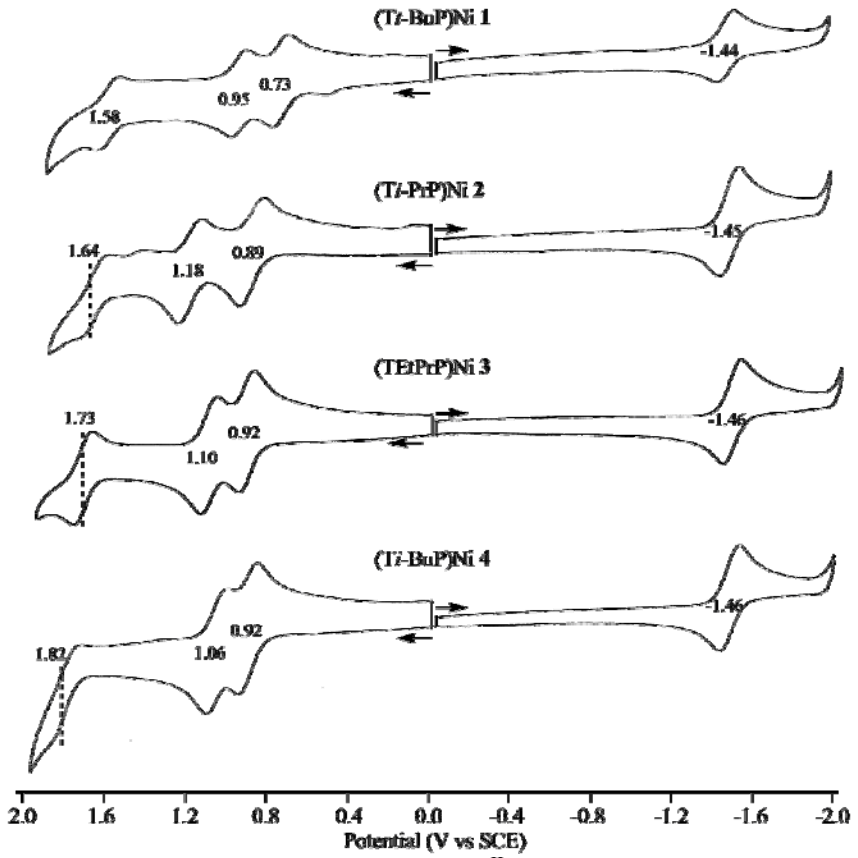

Figure 1. Cyclic voltammograms of tetraalkyl Ni^{II} porphyrins in PhCN containing 0.1 M TBAP, scan rate = 0.1 V/s.

Table 1. Half-wave potential (V vs SCE) of related Ni and Cu porphyrins in PhCN, 0.1 M TBAP.

Compound	Oxidation			Reduction		H-L gap
	$M^{II/III}$	Macrocycle		Macrocycle		
(T*t*-Bu P)Ni **1**	1.58	0.95	0.73	-1.44	-1.93	2.17
(T*i*-Pr P)Ni **2**	1.64	1.18	0.89	-1.45	-1.95	2.34
(TEtPr P)Ni **3**	1.73	1.10	0.92	-1.46	-1.95	2.38
(T*i*-Bu P)Ni **4**	1.82	1.06	0.92	-1.45		2.37
(OMTPP)Ni[d]	1.63	0.90	0.74	-1.48	-1.80	2.22
(TC_6TPP)Ni[d]	1.56	0.90	0.73	-1.50	-1.83	2.23
(OETPP)Ni	1.70	0.78	0.78	-1.51	-1.83	2.29
(DPP)Ni	1.64	0.84	0.84	-1.24	-1.67	2.08
(TPP)Ni	1.83	1.13	1.13	-1.26		2.39
(OEP)Ni[5,18]	1.88	1.21	0.78	-1.37		2.15
(OETPP)Cu	2.00[a]	0.97	0.46	-1.46	-1.90	1.92
(DPP)Cu	1.88	0.94	0.54	-1.22	-1.86	1.76
(TPP)Cu	(2.47)[c]	1.33	1.03	-1.28	-1.75	2.31
(OEP)Cu[b]		1.25[37]	0.75[37]	-1.46[38]		2.21

[a]Peak potential at scan rate of 0.1 V/s; [b]Data obtained in CH_2Cl_2, containing 0.1 M TBAP; [c]Predicted $E_{1/2}$ value (see text and Figure 5). [d]Oxidation potentials taken from reference 17.

The overall oxidative behavior of the strongly ruffled porphyrin (T*t*-BuP)Ni **1** closely resembles that which was previously described for the strongly saddled porphyrins,[18] (OMTPP)Ni^{II} and (TC_6PP)Ni^{II} (where OMTPP = the dianion of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphyrin and TC_6PP = 2,3,7,8,12,13,17,18-tetracyclohexenyl-5,10-15-20-tetraphenylporphyrin) in the same solvent (PhCN). All three porphyrins are oxidized at experimentally identical potentials of 0.73-0.74 V and all three porphyrins also have very similar $E_{1/2}$ values for the second and third redox process. This is true despite differences in both the alkyl and aryl *meso*-

substituents on the macrocycles of (T*t*-BuP)Ni **1**, (OMTPP)Ni and (TC_6TPP)Ni and in the type of nonplanar structure (ruffled for **1**[35] versus saddled for the other two compounds[7,39]).

Previous studies of porphyrin substituent effects have shown that changes in $E_{1/2}$ are influenced by electronic effect of substituents on the *meso* and β pyrrole positions of the macrocycle[3] as well as by conformational distortion of the macrocycle induced by crowding at the porphyrin periphery through *peri* interactions.[12] For instance, (OETPP)Ni is substantially easier to oxidize than (TPP)Ni (see Table 1) because of its saddle conformation and yields a complex postulated as a high spin Ni^{II} π cation radical.[22] The more facile macrocycle oxidation of **1** as compared to **2**, **3** or **4** is consistent with the strongly ruffled macrocycle of (T*t*-BuP)Ni that results from steric clashes between the substituents (*t*-Bu) and the adjacent pyrrole rings.[40,41]

The potential difference ($\Delta E_{1/2}$) between the first two oxidations of the tetraaryl-substituted porphyrins ranges from 140 to 290 mV and follows the order: (T*i*-BuP)Ni **4** (140 mV) < (TEtPrP)Ni **3** (180 mV) < (T*t*-BuP)Ni **1** (220 mV) < (T*i*-PrP)Ni **2** (290 mV), and there is no apparent correlation with nonplanarity of the porphyrin macrocycle. This suggests that other factors contribute to the $\Delta E_{1/2}$ differences between the first two oxidations, such as the type of dication formed (a_{1u} versus a_{2u}) or the anion binding affinity of the dication.[12] Interestingly, however, the reversible metal-centered $Ni^{II/III}$ reactions of **1-4** can be seen to shift to more positive potentials with increased nonplanar deformation (1.82 V for **4** versus 1.58 V for **1**). Given the similar electron donating/withdrawing effects of the substituents (as shown by the identical reduction potentials for **1-4**) this may suggest an effect of nonplanarity on the $Ni^{II/III}$ reactions.

II. Effect of Solvent on the $Ni^{II/III}$ Processes in Nonplanar Nickel Tetraalkylporphyrins. As discussed above, the $Ni^{II/III}$ process is observed only after the two one-electron ring-centered abstractions in PhCN. The first one-electron oxidation leads to a Ni^{II} π-cation radical whose UV-visible spectrum exhibits a decreased intensity Soret band and a broad band in the visible region of the spectrum. The same type of spectral changes are seen for all four tetraalkylporphyrins in PhCN, an example of which is shown in Figure 2a for (TEtPrP)Ni **3** during controlled-potential oxidation at 1.0 V in a thin-layer cell.

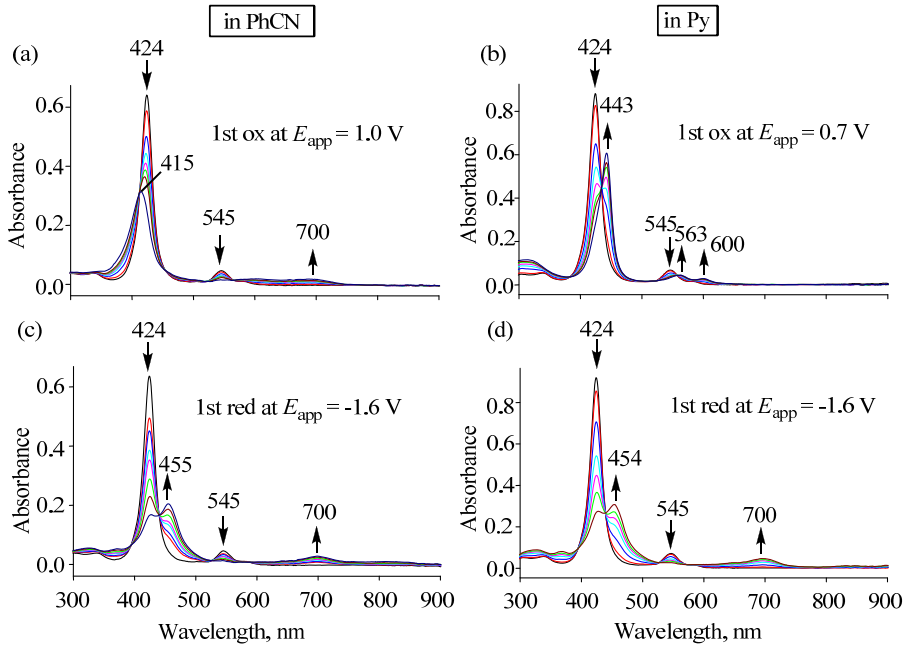

Figure 2. UV-visible spectral changes of (TEtPrP)Ni **3** upon the (a) first oxidation in PhCN, (b) first reduction in PhCN, (c) first oxidation on pyridine and (d) first reduction in pyridine containing 0.1 M TBAP.

As earlier demonstrated for other Ni^{II} porphyrins,[23] the site for the first oxidation of (TEtPrP)Ni **3** is quite different when the reaction is carried out in pyridine because this solvent coordinates to the singly oxidized form of the compound. Under these conditions,

the Soret band of neutral (TEtPrP)Ni **3** at 424 nm decreases in intensity while a new well-defined Soret band grows in at 443 nm for the singly oxidized species (see Figure 2b). At the same time, the Q band of Ni^{II} at 545 nm disappears and two well-defined new Q bands grow in at 563 and 600 nm. There is no broad band between 600 and 700 nm, indicating the lack of a π-cation radical. This type of spectral change suggests that the oxidation in pyridine has occurred at the central metal ion rather than at the porphyrin macrocycle. Singly oxidized (T*t*-BuP)Ni **1**, (T*i*-PrP)Ni **2** and (T*i*-BuP)Ni **4** exhibit similar spectral changes as does (TEtPrP)Ni **3** in pyridine. A summary of the UV-visible bands for the neutral and singly oxidized tetraalkylporphyrins in these two solvents is given in Table 2. The shift in the site of electron transfer upon change of the solvent from PhCN to pyridine has been well documented in the literature[23] and is due to coordination of pyridine to the singly oxidized form of the porphyrin.

Examples of the UV-vis spectral changes for reduction of (TEtPrP)Ni **3** in the two solvents are provided in Figures 2c and 2d. It should be noted that almost exactly the same UV-visible spectral changes are seen upon reduction of all four tetraalkylporphyrins whether the solvent is PhCN or Py.

Table 2. Absorption maxima (λ_{max}, nm) of tetraalkyl nickel porphyrins and their singly oxidized products in PhCN and Py containing 0.1 M TBAP.

Compound	In PhCN				In Py			
	$(TRP)Ni^{II}$		$[(TRP)Ni^{II}]^{+\cdot}$		$(TRP)Ni^{II}$		$[(TRP)Ni^{III}(Py)_2]^{+}$	
	Soret	Visible	Soret	Visible	Soret	Visible	Soret	Visible
(T*t*-BuP)Ni **1**	455	584, 622	422	778	452	583, 625	469	596, 646
(T*i*-PrP)Ni **2**	426	550, 583	413	689	424	548, 589	445	571, 608
(TEtPrP)Ni **3**	424	545, 583	415	700	424	545, 584	443	563, 600
(T*i*-BuP)Ni **4**	421	539, 582	411	688	421	542, 582	441	560, 601

III. Generation of the Cu^{III} Dication for highyl nonplanar (DPP)Cu and (OETPP)Cu. The electrochemistry of (TPP)Cu, (DPP)Cu and (OETPP)Cu was also investigated and cyclic voltammograms of these three compounds in PhCN containing 0.1 M TBAP are shown in Figure 3. Two reductions are observed for each porphyrin, as expected, and two oxidations are also seen for (TPP)Cu. Surprisingly, three oxidation processes are seen for (DPP)Cu and (OETPP)Cu, the latter of which has never before been reported.

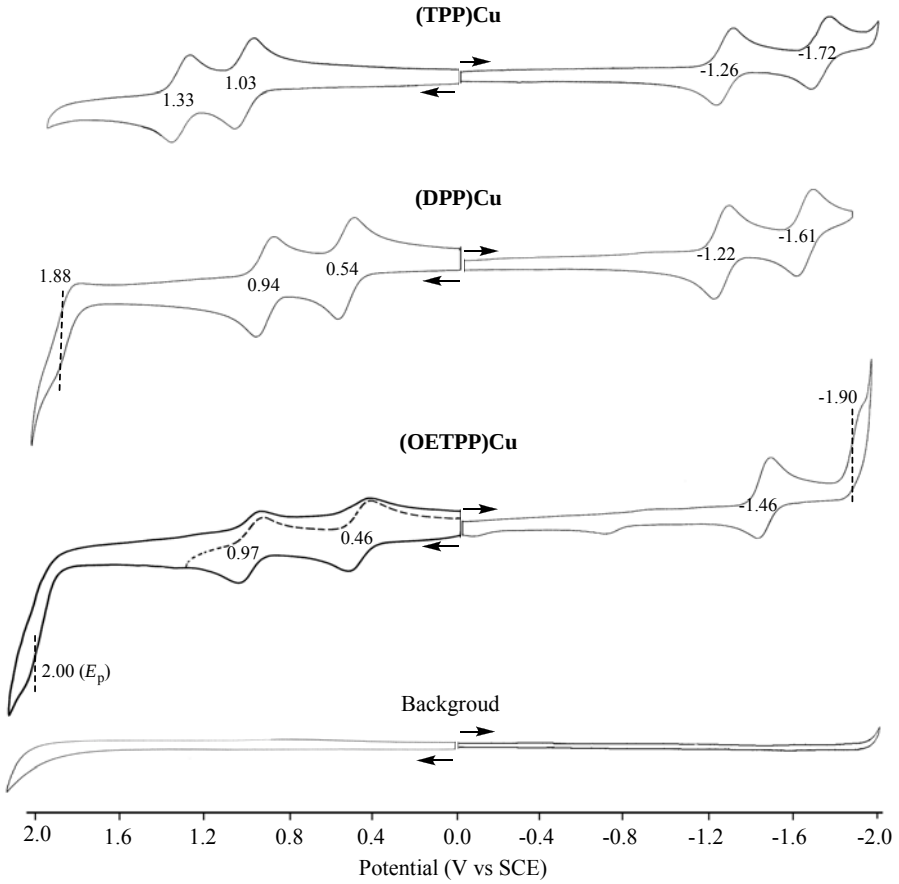

Figure 3. Cyclic voltammograms of (TPP)Cu, (DPP)Cu, (OETPP)Cu and solvent background in PhCN, 0.1 M TBAP. Scan rate = 0.1 V/s.

All four redox processes of (TPP)Cu are assigned as macrocycle-centered electron transfers to give a porphyrin π-anion radical and dianion on reduction and a porphyrin π-

cation radical and dication on oxidation.[3] The first two reductions and first two oxidations of (DPP)Cu and (OETPP)Cu are also centered at the conjugated π ring system of the porphyrin, with half-wave potentials being shifted negatively by about 500 mV as compared to (TPP)Cu due to the non-planarity of these two macrocycles (see exact $E_{1/2}$ values in Table 1).

The third oxidation of (DPP)Cu and (OETPP)Cu might at first be rationalized in terms of a solvent impurity or perhaps by formation of an isoporphyrin. However, the utilized solvent background is "clean" until beyond 2.00 V vs SCE (see Figure 3) and there is no evidence for coupled chemical reactions and formation of an isoporphyrin as indicated by variable scan rate measurements, low temperature measurements and multiple measurements on the same compounds taken with different batches of solvent. Thus, a more likely interpretation would be a metal-centered oxidation as is observed for the nickel porphyrins described in detail above.

The conversion of Cu^{II} to Cu^{III} in the third oxidation of (DPP)Cu and (OETPP)Cu is also strongly suggested by a comparison of the measured $E_{1/2}$ values for this process with redox potentials for the $M^{II/III}$ reaction of other transition metal porphyrins that have the same macrocycles, namely (DPP)M^{II} and (OETPP)M^{II}, where M = Fe, Co and Ni. One might expect to see a linear relationship between the third-ionization potential of the central metal ion and $E_{1/2}$ for the $M^{II/III}$ processes of the (DPP)M and (OETPP)M complexes, and this is exactly what is observed.

Examples of cyclic voltammograms are shown in Figure 4 for the (DPP)M^{II} derivatives containing Fe, Co, Ni and Cu while plots of the measured $E_{1/2}$ values for the $M^{II/III}$ reaction of the four porphyrins vs. the third ionization potential of the central metal

are shown in Figure 5a for (DPP)M^{II} and Figure 5b for (OETPP)M^{II}. Linear relationships are observed for both series of compounds using the third ionization potential[42] of the central metal ion (in eV) and newly measured $E_{1/2}$ values of the earlier characterized Fe, Co, Ni and Cu derivatives of (DPP)M and (OETPP)M in PhCN. A third oxidation is not observed for (TPP)Cu under the same solution conditions, but extrapolation of the linear relationship in Figure 5c for (TPP)M^{II} where M = Au, Fe, Co and Ni to the third ionization potential of Cu(II) gives a predicted half wave potential of 2.47 V for the $Cu^{II/III}$ process of (TPP)Cu in PhCN. This third oxidation cannot be observed experimentally because of the positive potential limit of the solvent.

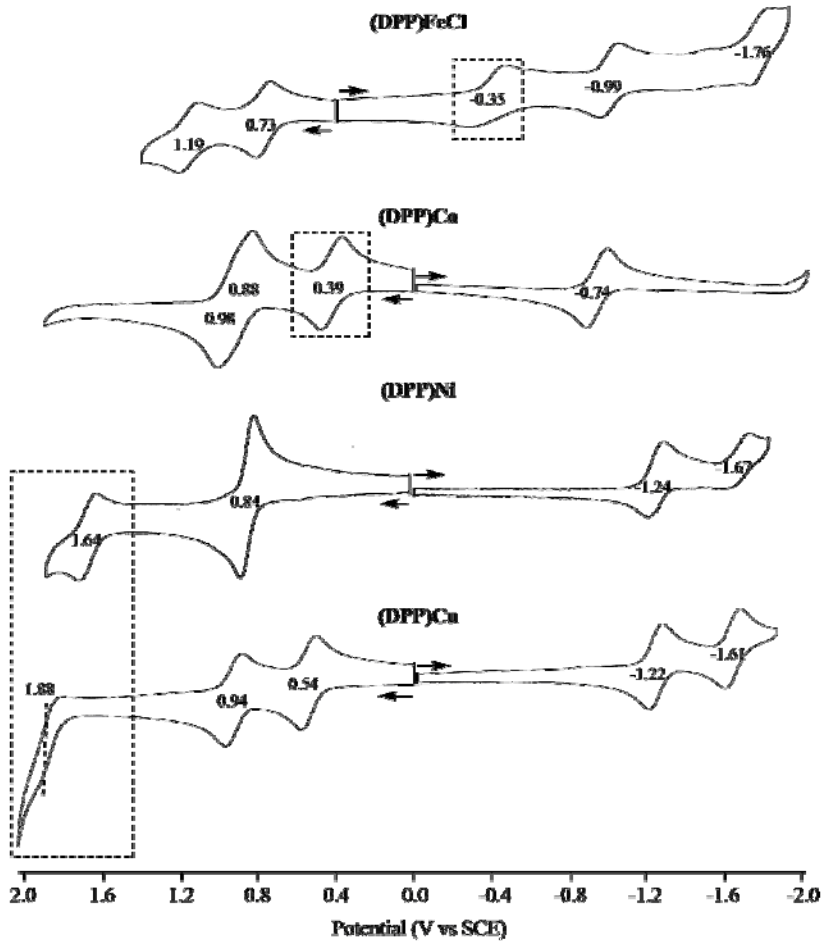

Figure 4. Cyclic voltammograms of (DPP)M in PhCN, 0.1 M TBAP where M = $Fe^{III}Cl$, Co^{II}, Ni^{II} and Cu^{II}. Scan rate = 0.1 V/s. The M^{II}/M^{III} processes are "boxed" in the figure.

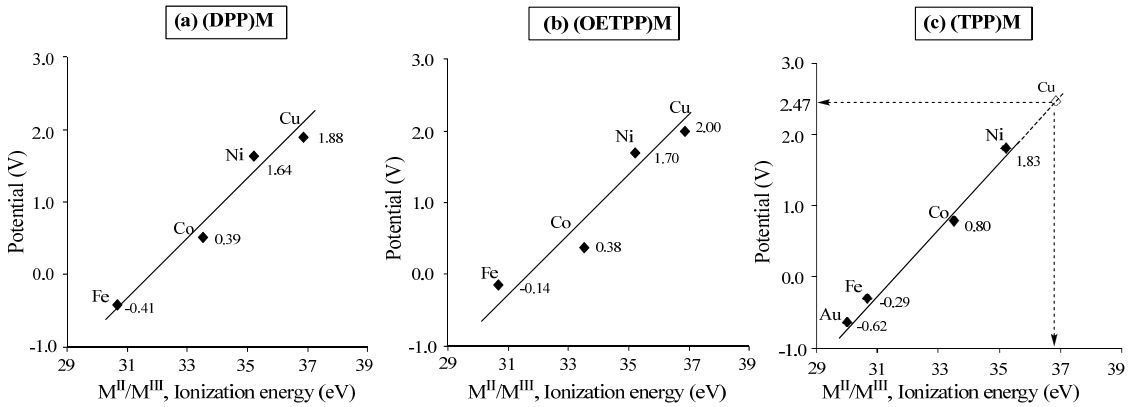

Figure 5. Correlation between gas phase ionization energies for $M^{II/III}$ and the $M^{II/III}$ redox process of (a) (DPP)M, (b) (OETPP)M and (c) (TPP)M in PhCN, 0.1 M TBAP (see Table 1 for potential). The ionization energies are taken from reference [42]. The $Cu^{II/III}$ process of (TPP)Cu is predicted to occur at 2.47 V based on the correlation in Figure 5c.

The data in Figures 3 and 5 suggests that a Cu(II)/Cu(III) process should be observed for other copper porphyrins under solution conditions where more positive potentials might be accessible. This possibility will be investigated in future studies with different solvent/supporting electrolyte combinations.

ACKNOWLEDGEMENT

We gratefully acknowledge support from the Robert A. Welch Foundation (K.M.K., Grant E-680), the Science Foundation Ireland (P.I. 09/IN.1/B2650) and the US National Institutes of Health (K.M.S. CA132861). C.J.M. acknowledges a 2013 Investigador Award from the Fundação para a Ciência e a Tecnologia, Portugal.

REFERENCES

(1) Kadish, K. M.; Smith, K. M.; Guilard, R. *The Porphyrin Handbook*; Academic Press: San Diego, 2000, 2003; Vol. 1-20.

(2) Kadish, K. M.; Smith, K. M.; Guilard, R. *Handbook of Porphyrin Science*; World Scientific: Singapore, 2010-2014; Vol. 1-35.

(3) Kadish, K. M.; Van Caemelbecke, E.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 8, p 1-114.

(4) Kadish, K. M.; Davis, D. G.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1014-1016.

(5) Fuhrhop, J.-H.; Kadish, K. M.; Davis, D. G. *J. Amer. Chem. Soc.* **1973**, *95*, 5140-5147.

(6) Kadish, K. M.; Royal, G.; Van Caemelbecke, E.; Gueletti, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 9, p 1-220.

(7) Sparks, L. D.; Medforth, C. J.; Park, M. S.; Chamberlain, J. R.; Ondrias, M. R.; Senge, M. O.; Smith, K. M.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 581-592.

(8) Ogura, H.; Yatsunyk, L.; Medforth, C. J.; Smith, K. M.; Barkigia, K. M.; Renner, M. W.; Melamed, D.; Walker, F. A. *J. Am. Chem. Soc.* **2001**, *123*, 6564-6578.

(9) Medforth, C. J.; Senge, M. O.; Smith, K. M.; Sparks, L. D.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 9859-9869.

(10) Shelnutt, J. A.; Medforth, C. J.; Berber, M. D.; Barkigia, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1991**, *113*, 4077-4087.

(11) Senge, M. O. *Chem. Commun. (Cambridge, U. K.)* **2006**, 243-256.

(12) Kadish, K. M.; Lin, M.; Van Caemelbecke, E.; De Stefano, G.; Medforth, C. J.; Nurco, D. J.; Nelson, N. Y.; Krattinger, B.; Muzzi, C. M.; Jaquinod, L.; Xu, Y.; Shyr, D. C.; Smith, K. M.; Shelnutt, J. A. *Inorg. Chem.* **2002**, *41*, 6673-6687.

(13) Kadish, K. M.; Van Caemelbecke, E.; D'Souza, F.; Medforth, C. J.; Smith, K. M.; Tabard, A.; Guilard, R. *Inorg. Chem.* **1995**, *34*, 2984-2989.

(14) Guilard, R.; Perie, K.; Barbe, J.-M.; Nurco, D. J.; Smith, K. M.; Van Caemelbecke, E.; Kadish, K. M. *Inorg. Chem.* **1998**, *37*, 973-981.

(15) Kadish, K. M.; Van Caemelbecke, E.; D'Souza, F.; Lin, M.; Nurco, D. J.; Medforth, C. J.; Forsyth, T. P.; Krattinger, B.; Smith, K. M.; Fukuzumi, S.; Nakanishi, I.; Shelnutt, J. A. *Inorg. Chem.* **1999**, *38*, 2188-2198.

(16) Song, Y.; Haddad, R. E.; Jia, S.-L.; Hok, S.; Olmstead, M. M.; Nurco, D. J.; Schore, N. E.; Zhang, J.; Ma, J.-G.; Smith, K. M.; Gazeau, S.; Pecaut, J.; Marchon, J.-C.; Medforth, C. J.; Shelnutt, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 1179-1192.

(17) Shelnutt, J. A.; Song, X.-Z.; Ma, J.-G.; Jia, S.-L.; Jentzen, W.; Medforth, C. J. *Chem. Soc. Rev.* **1998**, *27*, 31-42.

(18) Kadish, K. M.; Van Caemelbecke, E.; Boulas, P.; D'Souza, F.; Vogel, E.; Kisters, M.; Medforth, C. J.; Smith, K. M. *Inorg. Chem.* **1993**, *32*, 4177-4178.

(19) Kadish, K. M.; Van Caemelbecke, E.; D'Souza, F.; Medforth, C. J.; Smith, K. M.; Tabard, A.; Guilard, R. *Organometallics* **1993**, *12*, 2411-2413.

(20) Kadish, K. M.; Li, J.; Van Caemelbecke, E.; Ou, Z.; Guo, N.; Autret, M.; D'Souza, F.; Tagliatesta, P. *Inorg. Chem.* **1997**, *36*, 6292-6298.

(21) Sandusky, P. O.; Salehi, A.; Chang, C. K.; Babcock, G. T. *J. Am. Chem. Soc.* **1989**, *111*, 6437-6439.

(22) Renner, M. W.; Barkigia, K. M.; Melamed, D.; Gisselbrecht, J.-P.; Nelson, N. Y.; Smith, K. M.; Fajer, J. *Res. Chem. Intermed.* **2002**, *28*, 741-759.

(23) Seth, J.; Palaniappan, V.; Bocian, D. F. *Inorg. Chem.* **1995**, *34*, 2201-2206.

(24) Johnson, E. C.; Niem, T.; Dolphin, D. *Can. J. Chem.* **1978**, *56*, 1381-1388.

(25) Kadish, K. M.; Morrison, M. M. *Inorg. Chem.* **1976**, *15*, 980-982.

(26) Guilard, R.; Gros, C. P.; Barbe, J.-M.; Espinosa, E.; Jerome, F.; Tabard, A.; Latour, J.-M.; Shao, J.; Ou, Z.; Kadish, K. M. *Inorg Chem* **2004**, *43*, 7441-7455.

(27) Ou, Z.; Shao, J.; Zhao, H.; Ohkubo, K.; Wasbotten, I. H.; Fukuzumi, S.; Ghosh, A.; Kadish, K. M. *J. Porphyrins Phthalocyanines* **2004**, *8*, 1236-1247.

(28) Fox, J. P.; Ramdhanie, B.; Zareba, A. A.; Czernuszewicz, R. S.; Goldberg, D. P. *Inorg. Chem.* **2004**, *43*, 6600-6608.

(29) Luobeznova, I.; Simkhovich, L.; Goldberg, I.; Gross, Z. *Eur. J. Inorg. Chem.* **2004**, 1724-1732.

(30) Tangen, E.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8117-8121.

(31) Wasbotten, I. H.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2002**, *124*, 8104-8116.

(32) Ghosh, A.; Wondimagegn, T.; Parusel, A. B. J. *J. Am. Chem. Soc.* **2000**, *122*, 5100-5104.

(33) Will, S.; Lex, J.; Vogel, E.; Schmickler, H.; Gisselbrecht, J.-P.; Haubtmann, C.; Bernard, M.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 357-361.

(34) Paolesse, R. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, 2000; Vol. 2, p 201-232.

(35) Senge, M. O.; Bischoff, I.; Nelson, N. Y.; Smith, K. M. *J. Porphyrins Phthalocyanines* **1999**, *3*, 99-116.

(36) Ema, T.; Senge, M. O.; Nelson, N. Y.; Ogoshi, H.; Smith, K. M. *Angew. Chem.* **1994**, *106*, 1951-1953.

(37) Stolzenberg, A. M.; Schussel, L. J. *Inorg. Chem.* **1991**, *30*, 3205-3213.

(38) Chang, C. K.; Barkigia, K. M.; Hanson, L. K.; Fajer, J. *J. Am. Chem. Soc.* **1986**, *108*, 1352-1354.

(39) Barkigia, K. M.; Renner, M. W.; Furenlid, L. R.; Medforth, C. J.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3627-3635.

(40) Senge, M. O.; Ema, T.; Smith, K. M. *J. Chem. Soc., Chem. Commun.* **1995**, 733-734.

(41) Jentzen, W.; Simpson, M. C.; Hobbs, J. D.; Song, X.; Ema, T.; Nelson, N. Y.; Medforth, C. J.; Smith, K. M.; Veyrat, M.; et, a. *J. Am. Chem. Soc.* **1995**, *117*, 11085-11097.

(42) Lide, D. R. *Chemical Rubber Company handbook of chemistry and physics*; 79th ed.; CRC Press: Florida, 1998.

Synopsis

Impact of Substituents and Nonplanarity on Nickel and Copper Porphyrin Electrochemistry – First Observation of a Cu(II)/Cu(III) Reaction in Nonaqueous Media

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A series of *meso*-tetraalkyl Ni^{II} porphyrins was electrochemically investigated along with Ni^{II} and Cu^{II} derivatives of dodecaphenylporphyrin and octaethyltetraphenylporphyrin. Each investigated porphyrin exhibits three oxidations, the first two of which are macrocycle centered to give the porphyrin dication followed by an $M^{II/III}$ process at more positive potentials.