

## Porphodimethene–Porphyrin Interconversion: A Tetrapyrrolic Redox-Switchable Macrocycle

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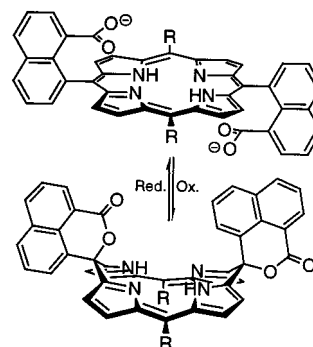
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Nucleophilic substituents placed in proximity to the *meso*-carbon positions of a porphyrin ring influence the electronics of the macrocycle, and these interactions can be detected by both electrochemical and EPR measurements.<sup>1</sup> For example, the NH group in *meso*-(*o*-anilido)porphyrins are located close enough to the macrocycle to significantly alter the electrochemistry of the ring.<sup>1a</sup> This interplay between nucleophiles and the *meso*-carbon positions of the porphyrin macrocycle may have many broad implications among them porphyrin degradation in metal assisted oxidation reactions and natural heme catabolism.<sup>2,3</sup> In addition, the decomposition of mono-functionalized naphthoic acid porphyrins to afford oxaporphyrins has been reported by Chang, and this breakdown appeared to be initially induced by an intramolecular attack of the carboxylic acid group on the *meso*-carbon to form an isoporphyrin followed by further air oxidation to the oxaporphyrin.<sup>3</sup> Isolation and characterization of the intermediates has likely been hampered by the presence of only one functional group since the resultant isoporphyrin products are quite unstable. As well as perhaps producing new intermediates, the simultaneous interaction of two functional groups fixed at the 5- and 15-positions of a porphyrin offers the ability to form a stable porphodimethene product rather than the isoporphyrin. Herein, we report the first reversible porphodimethene-porphyrin interconversion mediated by nucleophilic substituents proximal to the *meso*-carbon atoms of a tetrapyrrolic macrocycle.

We recently described the syntheses of *trans*-porphyrins bearing two 8-carboxy functionalized naphthalene spacer.<sup>4</sup> When these compounds are exposed to air for prolonged periods or treated with oxidizing agents such as DDQ or [Fe(Cp)<sub>2</sub>]PF<sub>6</sub>, a decay of both metalated and unmetalated porphyrins is repeatedly observed. The stability of the porphyrins is strongly dependent on several factors including the electronic and steric nature of the *meso* aryl substituents in addition to the identity of the metal ion incorporated into the macrocycle. Degradation of the porphyrins can be attributed to the proximity of the carboxylate groups to the porphyrin plane allowing a direct interaction between the carboxylate oxygens and respective *meso* sp<sup>2</sup>-carbon atoms (Scheme 1). As illustrated in the solid-state structure of the mesityl-substituted dipotassium salt derivatives, the separation between these atoms range from 2.98 to 3.50 Å.<sup>5</sup>

Accordingly, the electrochemical attributes of some selected derivatives were examined (Table 1). In sharp contrast to the both mono *meso*-(*o*-anilido) and *meso*-carboxynaphthalene derivatives, compounds 1–6 do not exhibit a reversible 2e<sup>-</sup> oxidation, even at higher scan rates (400 mV/s); instead an irreversible oxidation wave is evident, significantly shifted to lower potentials in comparison to the reversible oxidation waves normally found in tetraaryl porphyrins. Nevertheless, in analogy to the tetraaryl porphyrins, the oxidation potentials of 1–6 are profoundly

**Scheme 1.** Schematic Diagram of the Porphyrin–Porphodimethene Conversion with the Unmetalated Macrocycles (Structure of 1–3 Is Shown at Top while 3a Is Depicted at the Bottom)



**Table 1.** Electrochemical Oxidation Potentials of 1–7<sup>a</sup>

R	M	$E_{p(ox)}$ (mV)	solvent
3,4,5-(OMe) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (1)	—	491	MeOH
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (2)	—	455	MeOH
3,5-(Bu) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (3)	—	516	MeOH
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (4)	Cu	443	MeOH
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (5)	Zn	286	MeOH
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (6)	Zn	736	CH <sub>2</sub> Cl <sub>2</sub>
2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (7)	—	978/1340 [ $E_{1/2}^{ox}$ (1)/ $E_{1/2}^{ox}$ (2)]	CH <sub>2</sub> Cl <sub>2</sub>

<sup>a</sup> 1–5:  $\alpha\beta$ -dipotassium salt. 6:  $\alpha\alpha$ -free acid. 7:  $\alpha\beta$ -dimethylester. Potentials (mV vs SCE) were measured with a Pt disk working electrode, a Pt wire counter electrode, an electrolyte (TBAH) concentration of 0.1 M, and a scan rate of 100 mV/s

influenced by the electronic properties of both the aryl substituents and the central metal ion,<sup>6</sup> and their unusual redox behavior with regards to tetraaryl porphyrins is undoubtedly governed by the carboxylate groups bound at 8-position of the naphthalene spacer.

Hence, if the reactive carboxylate is protected as the ester as exemplified in 7, the cyclic voltammogram of the porphyrin shifts to higher potentials and exhibits two reversible oxidation waves. Although the ester groups in 7 are in proximity to the porphyrin plane, the increased steric strain and reduced nucleophilicity of the carbonyl oxygen does not allow for extensive oxygen–porphyrin interactions. Even without the ester protection, a reduction in the nucleophilicity of the carboxylate oxygen induces a shift to higher potential for the first oxidation as highlighted by the 450 mV increase for  $\alpha\alpha$  free acid 6 relative to the  $\alpha\beta$ -dipotassium salt 5 (R = mesityl, M = Zn for both).<sup>7</sup> Unfortunately, due to the insolubility of the free acid  $\alpha\beta$ -atropisomers in common solvents no data is currently available for these derivatives.<sup>5</sup>

Given the exceptionally low oxidation potential of 5 (+286 mV), simple reagents should be capable of oxidizing the porphyrin macrocycle and reaction of the ( $\alpha\beta$ ) dipotassium salt 5 in MeOH with an excess of DDQ instantly affords the precipitation of a bright orange material in 89% yield. In comparison to the porphyrin 5 (430 nm), the UV-spectrum of the oxidation product 5a displays a significant bathochromic shift (466 nm) of the former Soret band accompanied by a decrease in intensity [log  $\epsilon$ : 5.63 (5); 5.21 (5a)] and a loss of the Q-bands. On the basis of the <sup>1</sup>H NMR spectrum of the oxidized product, the tetrapyrrolic

(6) Felton, R. H. in Dolphin, D. *The Porphyrins*; Academic Press: New York, 1978; Vol V, pp 53–125.

(7) Due to solubility problems, the potentials of the porphyrin dipotassium salts were all measured in methanol, while dichloromethane was used for 6 and 7. The large shift to higher potentials witnessed from 6 to 5 may, in part, arise from solvent effects.

(1) (a) El-Kasmi, A.; Lexa, D.; Maillard, P.; Momenteau, M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1991**, *113*, 1586. (b) Kalsbeck, W. A.; Seth, J.; Bocian, D. F. *Inorg. Chem.* **1996**, *35*, 7935. (c) Vangberg, T.; Ghosh, A. *J. Am. Chem. Soc.* **1998**, *120*, 6227 and references therein.

(2) Balch, A. L.; Koerner, R. Latos-Grażyński, L.; Noll, B. C. *J. Am. Chem. Soc.* **1996**, *118*, 2760 and references therein.

(3) Chang, C. K.; Avilés, G.; Bag, N. *J. Am. Chem. Soc.* **1994**, *116*, 12127.

(4) Harmjanz, M.; Scott, M. J. *Chem. Commun.* **2000**, 397.

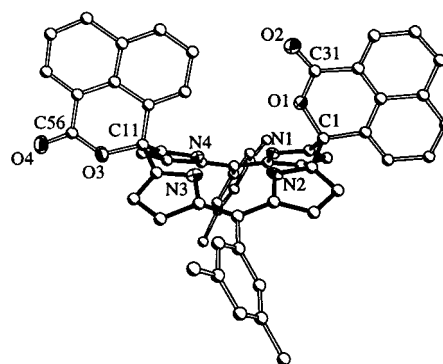
(5) Harmjanz, M.; Scott, M. J. *Inorg. Chem.* **2000**, submitted.

macrocycle remains intact, but the pyrrolic protons shift upfield [ $\delta$ : 8.54, 8.42 ppm (**5**); 6.32, 6.03 ppm (**5a**)], intimating a disruption of the electron delocalization within the macrocyclic ring system. Using similar procedures, the metalated (Zn)  $\alpha$ -free acid **6** and the unmetalated ( $R = 3,5\text{-}(\text{Bu}^t)_2\text{-C}_6\text{H}_3$ ) dipotassium salt **3** ( $\alpha\beta$  atropisomer) were also oxidized, and the orange products (**3a** and **6a** respectively) were isolated and fully characterized. In sharp contrast to common porphyrins, the resonances for the N–H protons in  $^1\text{H}$  NMR of the unmetalated derivative **3a** are drastically shifted downfield to 14.3 ppm, characteristic for porphodimethenes.<sup>4,8</sup> Evidently, the irreversible oxidation wave in the cyclic voltammograms of **1–6** can be attributed to an initial attack of the carboxy-oxygen at the *meso* carbons and subsequent intramolecular lactonization and formation of the corresponding porphodimethenes. While intermolecular nucleophilic *meso*-substitution and -addition reactions of oxidative activated and unactivated porphyrins have been widely examined,<sup>9</sup> to the best of our knowledge, an analogous intramolecular reaction has not been reported.

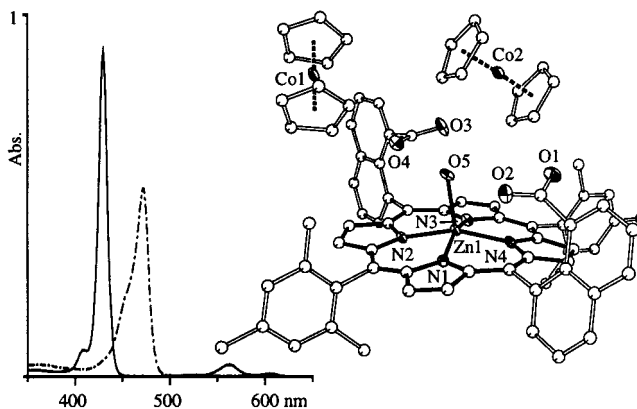
As illustrated in Figure 1,<sup>10</sup> the oxidative lactonization leads to the formation of a six membered ring whereby the two 1*H*,3*H*-naphtho[1,8-*cd*]pyrane-1-one groups are aligned in the expected *anti* position. Due to the  $\text{sp}^3$ -hybridized *meso* carbon atoms, the tetrapyrrolic skeleton adopts a strong rooflike conformation with an interplanar angle between the two dipyrromethene moieties of  $124.8^\circ$ , an angle comparable to those found in other unmetalated porphodimethenes.<sup>8,11</sup>

In an effort to reestablish the aromatic porphyrin system, we investigated the electrochemical behavior of the porphodimethenes. As an example, the *anti*-derivative **3a** undergoes an irreversible reduction at  $-1010$  mV and reoxidation at  $451$  mV (SCE).<sup>12</sup> The reduction of the metalated (Zn) *syn*-porphodimethene **6a** has also been achieved by chemical means through the addition of stoichiometric amounts of cobaltocene. The resulting porphyrin immediately precipitated out of the THF reaction mixture, affording ( $\alpha\alpha$ ) *trans*-8-carboxynaphthylporphyrin **8** as the dicobaltocenium salt in high yield.

Binding an axial water molecule, the coordination environment around the  $\text{Zn}^{2+}$  in the solid-state structure of **8** (Figure 2) can be best described as distorted square pyramidal with the Zn situated  $0.37$  Å above the  $\text{N}_4$  plane and an average Zn(1)–N bond length of  $2.07(1)$  Å.<sup>13</sup> To allow for a hydrogen-bonding interaction, the coordinated water molecule orients toward one of the carboxylate groups resulting in an O(5)–O(4) separation of  $2.762(6)$  Å.<sup>14</sup> Consequently, the N–Zn(1)–O(5) angles range from  $94.2(2)$  to  $107.0(2)^\circ$ . Due to electronic repulsions, the two  $-\text{CO}_2$  functions are slightly inclined back from the porphyrin



**Figure 1.** Diagram of **3a** (30% ellipsoids, carbons arbitrary radii). Hydrogen atoms and  $\text{Bu}^t$ -methyl-groups omitted for clarity.



**Figure 2.** Left: UV/vis spectrum of **6a** (dashed line;  $\text{CH}_2\text{Cl}_2$ ) and the cobaltocene reduced species **8** (solid line;  $\text{CH}_3\text{OH}$ ). Right: Diagram of **8** (30% ellipsoids, carbons arbitrary radii). Hydrogen atoms have been omitted for clarity.

plane. The two cobaltocenium counterions reside close to the naphthalenecarboxy functionalities with the central Co-ions situated  $5.74$  and  $6.14$  Å above the plane defined by the four pyrrolic nitrogen atoms.

In summary, the first example of a reversible, redox-controlled porphyrin–porphodimethene interconversion via a sequential intramolecular ring opening and closure reaction at the *meso* positions has been described. The respective oxidation potentials can be easily manipulated by the judicious choice of the aromatic residues as well as by the metal ion incorporated into the macrocycles. With regard to the carboxy functions at the naphthalene spacer, these potential recognition sites can be electrochemically and chemically activated and deactivated, offering many exciting possibilities for the design of novel redox switchable sensors or photosensitizers. Work is also in progress to further define these unique ring-opening reactions and investigate the redox behavior of the compounds in the presence of acids and bases.

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**Supporting Information Available:** Complete experimental procedures and characterization data for **3–6a**, **8** and X-ray structural details for **3a**, and **8** (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA003004C

(8) (a) Buchler, J. W.; Puppe, L. *Justus Liebigs Ann. Chem.* **1970**, *740*, 142. (b) Král, V.; Sessler, J. L.; Zimmerman, R. S.; Seidel, D.; Lynch, V.; Andrioletti, B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1055. (c) Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C.; Re, N. *J. Am. Chem. Soc.* **2000**, *122*, 5312. And references therein.

(9) For example: (a) Dolphin, D.; Felton, R. H.; Borg, D. C.; Fajer, J. *J. Am. Chem. Soc.* **1970**, *92*, 743. (b) Smith, K. M.; Barnett, G. H.; Evans, B.; Martynenko, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5953. (c) Senge, M. O.; Kalisch, W. W.; Bischoff, I. *Chem. Eur. J.* **2000**, *6*, 2721.

(10) Crystal data for **3a**·1.5THF:  $\text{C}_{76}\text{H}_{76}\text{N}_4\text{O}_{5.5}$ , fw = 1133.41, monoclinic,  $P2_1/n$ ,  $a = 15.2507(7)$  Å,  $b = 16.5894(8)$  Å, and  $c = 25.851(1)$  Å,  $\beta = 102.923(1)^\circ$ ,  $V = 6374.7(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.181$  g  $\text{cm}^{-3}$ , 6536 reflections of 8862 with  $I > 2(\sigma)I$ ,  $R_1 = 0.0804$ ,  $wR_2 = 0.2182$ .

(11) Harmjan, M.; Gill, H. S.; Scott, M. J. Manuscript in preparation.

(12) Benzonitrile, TBAH (0.1 M), vel = 100 mV/s, Pt<sub>w</sub>, Pt<sub>r</sub>, SCE.

(13) Crystal data for **8**·5.25MeOH:  $\text{C}_{85.25}\text{H}_{84}\text{N}_4\text{O}_{10.25}\text{Co}_2\text{Zn}$ , fw = 1511.79, monoclinic,  $P2_1/c$ ,  $a = 29.448(3)$  Å,  $b = 12.588(1)$  Å, and  $c = 21.842(2)$  Å,  $\beta = 107.913(2)^\circ$ ,  $V = 7704.1(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_{\text{calcd}} = 1.303$  g  $\text{cm}^{-3}$ , 6821 reflections of 10341 with  $I > 2(\sigma)I$ ,  $R_1 = 0.0867$ ,  $wR_2 = 0.1955$ .

(14) The short Zn–O(5) distance of  $2.075(6)$  Å may suggest some delocalization of a proton from the water to either of the carboxylates.