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## COMMUNICATION

Facile Electrosynthesis of  $\pi$ -Extended Porphyrins

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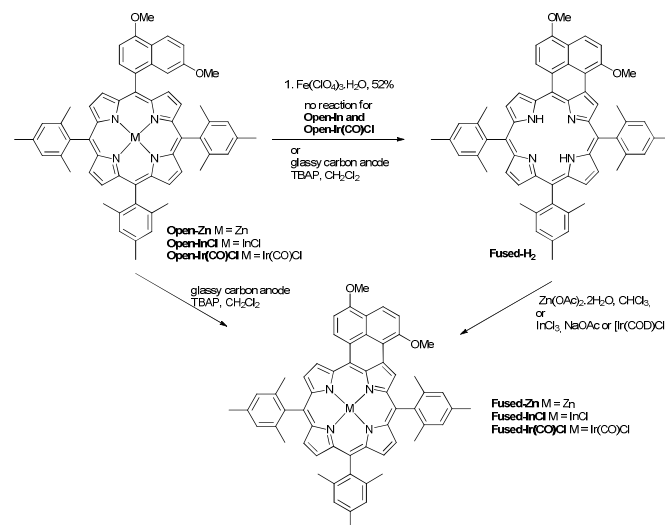
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The facile electrocatalysis of  $\pi$ -extended porphyrins is demonstrated for a series of Zn(II), In(III), Ir(III) and free-base *meso*-substituted derivatives containing 4,7-dimethoxynaphthalen-1-yl substituent. Electrochemical data suggest that, the overall process initially involves two stepwise one-electron oxidations, followed by an intramolecular oxidative aromatic coupling to give the electrooxidized  $\pi$ -extended porphyrin.

Both  $\pi$ -expanded and  $\pi$ -extended porphyrins have been widely used as building blocks for supramolecular and organic materials chemistry.<sup>1-8</sup> The intrinsically high electron-density of porphyrins is responsible for the fact that oxidative aromatic coupling<sup>9</sup> has recently become the most popular method for  $\pi$ -extension of these compounds.<sup>2,10</sup> Although numerous aromatic hydrocarbons and heterocycles have been fused with porphyrins over the last 20 years, many challenges still remain, the most important of which are an unpredictability of the reaction outcome, contamination from monochlorinated by-products (FeCl<sub>3</sub>)<sup>11</sup> and the lack of a successful fusion reaction with free-base porphyrin derivatives. As a matter of fact, despite the publication of hundreds of manuscripts on the topic, only Zn-, Cu- and Ni-complexes of porphyrins have been successfully oxidatively coupled.<sup>2,10-15</sup>

Further progress in this is methodology depends on cracking down the mechanism of this reaction. Various mechanisms have been proven to operate in oxidative aromatic coupling such as coupling of aryloxy radicals, radical substitution, and cation-radical dimerization.<sup>9</sup> Electrochemically driven oxidative aromatic coupling is a useful method which can afford products on the electrode surface without contamination<sup>16</sup> as it was recently demonstrated by Waldvogel and co-workers.<sup>17</sup> This approach was first applied to the synthesis of porphyrinoids by Sessler and Bucher.<sup>18</sup> At the same time electrochemistry is a unique tool to elucidate the order of steps in oxidative aromatic coupling. We envisioned that such electrochemical reaction described in our initial study for fusion of a nickel porphyrin<sup>19</sup> would also occur for porphyrins containing a variety of metal ions as well as for the free-base porphyrins where chemically induced fusion reactions have yet to be demonstrated. As

a test of this hypothesis, we set ourselves the goal to perform the electrocatalysis of  $\pi$ -extended porphyrins for four types of compounds: (a) an easily oxidizable formally four coordinate zinc(II) porphyrin, which we wished to directly electrocatalyze as a  $\pi$ -extended derivative without concomitant removal the Zn(II) central metal ion; (b) a five coordinate indium(III)-porphyrin, which possess a relatively high oxidation potential; (c) a six coordinate Ir(III) porphyrin which also possesses a high oxidation potential and (d) a free-base porphyrin, the latter of which has proven all but impossible to synthesis in its  $\pi$ -extended form from 'regular' free-base porphyrins using chemical methods.



**Scheme 1** Chemical and electrocatalysis synthesis of  $\pi$ -extended porphyrins.

We resolved to use the same basic architecture as was shown to be successful in chemical synthesis of the same  $\pi$ -extended porphyrins i.e. porphyrins possessing three mesityl groups and one 4,7-dimethoxynaphthalen-1-yl unit.<sup>11</sup> The rationale behind this choice was the possibility to compare properties of the chemically

fused products to that of the products generated by an electrochemically induced oxidation process. In the chemical fusion method, mixed-condensation afforded the porphyrin **Open-H<sub>2</sub>**, which was subsequently transformed into the zinc complex **Open-Zn**, which was then chemically oxidized with Fe(ClO<sub>4</sub>)<sub>3</sub> to afford **Fused-H<sub>2</sub>** in 52% yield.<sup>11</sup> As described previously, the Lewis acid character of Fe<sup>3+</sup> causes quantitative removal of zinc during oxidative aromatic coupling. The porphyrin **Fused-H<sub>2</sub>** was subsequently metallated following known procedures to afford the In(III), Zn(II) and Ir(III) complexes (Scheme 1).

Measured half-wave or peak potentials for reduction and oxidation of the tetra-mesitylporphyrin (**TMP**) and fused porphyrins in PhCN are summarized in Table 1 while the redox potentials in CH<sub>2</sub>Cl<sub>2</sub> are given in Table S1. These tables also include data for the related starting compounds with a single *meso*-naphthalene group.

**Table 1** Half-wave or Peak Potentials (V vs SCE) in PhCN, containing 0.1 M TBAP. Scan rate of 0.1 V/s

M	Ring	Oxidation		Reduction		H-L gap (V)
		2 <sup>nd</sup>	1 <sup>st</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	
H <sub>2</sub>	TMP	1.41	1.12	-1.19	-1.69	2.31
	Open	1.24 <sup>[b]</sup>	1.10	-1.19	-1.68	2.29
	Fused	1.01	0.71	-1.08	-1.56	1.79
Zn	TMP	1.18	0.82	-1.38	-	2.20
	Open	1.12	0.81	-1.36	-1.85	2.17
	Fused	0.85	0.53	-1.25	-1.71	1.78
Ni <sup>[a]</sup>	TMP	1.14	1.14	-1.30	-	2.44
	Open	1.14	1.14	-1.24	-1.84	2.38
	Fused	1.00	0.74	-1.20	-1.80 <sup>[b]</sup>	1.94
InCl	TMP	1.57	1.24	-1.05	-1.58	2.29
	Open	1.40 <sup>[b]</sup>	1.21	-1.01	-1.55	2.22
	Fused	1.13	0.85	-0.97	-1.46	1.82
Ir(CO)Cl	TMP	1.64	1.27	-1.17	-1.39	2.44
	Open	1.43 <sup>[b]</sup>	1.22	-1.15	-1.74	2.37
	Fused	0.85	0.53	-1.23	-1.69	1.76

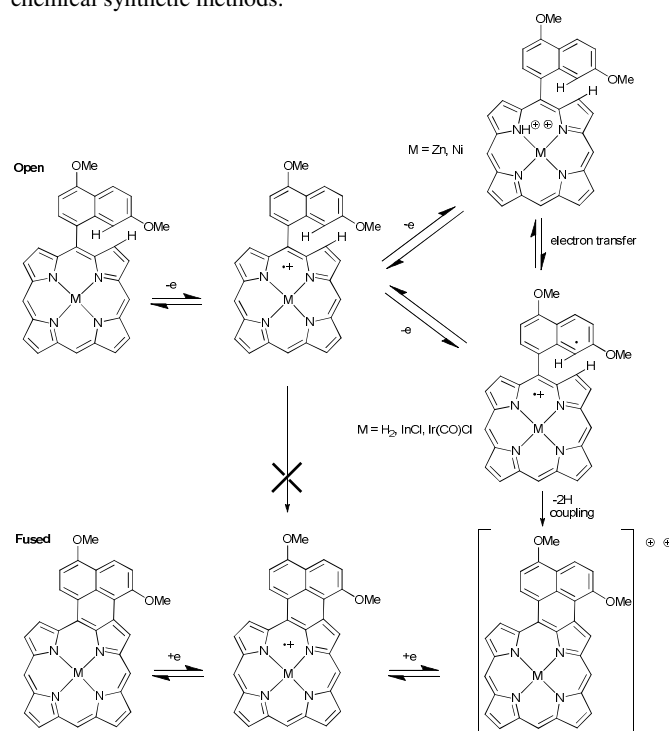
<sup>[a]</sup>Data Taken from ref. 19; <sup>[b]</sup>Peak potential at scan rate of 0.1 V/s.

The similarity in the first reduction and first oxidation potentials of compounds having the **TMP** and **Open** macrocycles is related to the similar substituent effects of the trimesityl and naphthalene groups and to the similar sites of electron transfer, which in this case is the conjugated  $\pi$ -ring system of the porphyrin. Similar potentials are not observed for the second oxidation of the **TMP** and **Open** macrocycle compounds where much larger differences are observed suggesting different sites of electron transfer for this reaction in the two series of compounds. The  $\Delta E_{1/2}$  between the **TMP** and **Open** porphyrin derivatives ranges from 170-210 mV in the case of the free-base, InCl and Ir(CO)Cl compounds to 60 mV in the case of the Zn(II) complexes.

As shown in Table 1, the chemically synthesized Zn(II) porphyrin with a  $\pi$ -extended system **Fused-Zn** is reversibly oxidized in two one-electron steps located at  $E_{1/2} = 0.53$  and  $0.85$  V in PhCN, 0.1 M TBAP. This compares to the **Open-Zn**, which exhibits two reversible one-electron oxidations at  $E_{1/2} = 0.81$  and  $1.12$  V under the same solution condition. The product of the one-electron oxidation of the **Open-Zn** is stable on the cyclic voltammetry time scale and it is also stable after holding the potential for 2 min at 1.05 V and then reversing the potential sweep direction to reduce the **Open** porphyrin  $\pi$ -radical cation to its neutral form again. This is shown by the top cyclic voltammogram in Figure S1a.

The second oxidation of **Open-Zn** also occurs on the porphyrin core followed by electron-transfer leading to bis-radical (Scheme 2). The doubly oxidized **Open-Zn** generated in PhCN at  $E_{1/2} = 1.12$  V is unstable on the cyclic voltammetry timescale of 0.10 V/s and undergoes a slow chemical conversion to the dication of the **Fused-Zn**, as demonstrated by the decreased current for the second oxidation on the return sweep and the appearance of a new cathodic peak at  $E_p = 0.48$  V (see Figure S1a).

Additional evidence for electro-synthesis of the  $\pi$ -extended porphyrin is given by the cyclic voltammogram in Figure S1b where the potential was held for 2 min at 1.50 V before initiating the scan in a negative direction. Under these conditions, a larger amount of the **Open-Zn** is consumed and the redox process associated with the electro-synthesized **Fused-Zn** at  $E_{1/2} = 0.51$  V exhibits an increased peak current, consistent with larger amounts of this material being formed at the electrode surface. A comparison of the cyclic voltammogram in Figure S1b with that of the chemically synthesized **Fused-Zn** in Figure S1c, shows clearly that the same chemical species has been formed by electro-synthesis in PhCN as by classical chemical synthetic methods.



**Scheme 2** Mechanism of electrochemical oxidative aromatic coupling.

In summary, electrochemical evidence suggest that, the mechanism for conversion of the **Open-Zn** to the **Fused-Zn** involves two one-electron oxidations followed by a radical coupling to give the **Fused-Zn** dication as shown in Scheme 2. This doubly oxidized porphyrin with an extended  $\pi$ -system is then reduced by two one-electron transfers at  $0.85$  and  $0.51$  V to give the final, neutral **Fused-Zn**. Both the first and second one-electron abstractions of the **Open-Zn** occur at the porphyrin core, which is governed by the order of electrochemical oxidation potentials (Table 1).

The spectroelectrochemistry (Fig. 1) gives evidence that the slightly different mechanism occurs in the case of the InCl derivatives where the **Open-InCl** porphyrin is converted to the



**Table of contents graphic and text:**

Free-base porphyrins as well as their iridium and indium complexes have been electrochemically coupled, leading to  $\pi$ -extended macrocycles..

