

Facile electrosynthesis of π -extended porphyrins†Cite this: *Chem. Commun.*, 2014,
50, 8864Received 14th April 2014,
Accepted 14th June 2014

DOI: 10.1039/c4cc02759k

www.rsc.org/chemcomm

Yuanyuan Fang,^a Dominik Koszelewski,^b Karl M. Kadish*^a and Daniel T. Gryko*^b

The facile electrosynthesis of π -extended porphyrins is demonstrated for a series of Zn(II), In(III), Ir(III) and free-base meso-substituted derivatives containing the 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 π -extended porphyrin.

Both π -expanded and π -extended porphyrins have been widely used as building blocks for supramolecular and organic materials chemistry.^{1–8} The intrinsically high electron-density of porphyrins is responsible for the fact that oxidative aromatic coupling⁹ has recently become the most popular method for π -extension of these compounds.^{2,10} 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 mono-chlorinated by-products (FeCl₃)¹¹ 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.^{2,10–15}

Further progress in this 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.⁹ Electrochemically driven oxidative aromatic coupling is a useful method which can afford products on the electrode surface without contamination¹⁶ as recently demonstrated by Waldvogel and co-workers.¹⁷ This approach

was first applied to the synthesis of porphyrinoids by Sessler and Bucher.¹⁸ 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 porphyrin¹⁹ would also occur for porphyrins containing a variety of metal ions as well as for the free-base porphyrins where chemically induced fusion reactions are yet to be demonstrated. As a test of this hypothesis, we set ourselves the goal to perform the electrosynthesis of π -extended porphyrins for four types of compounds: (a) an easily oxidizable formally four coordinate zinc(II) porphyrin, which we wished to directly electrosynthesize as a π -extended derivative without concomitant removal of the Zn(II) central metal ion; (b) a five coordinate indium(III)-porphyrin, which possesses 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 it is impossible to be synthesized in its π -extended form from 'regular' free-base porphyrins using chemical methods.

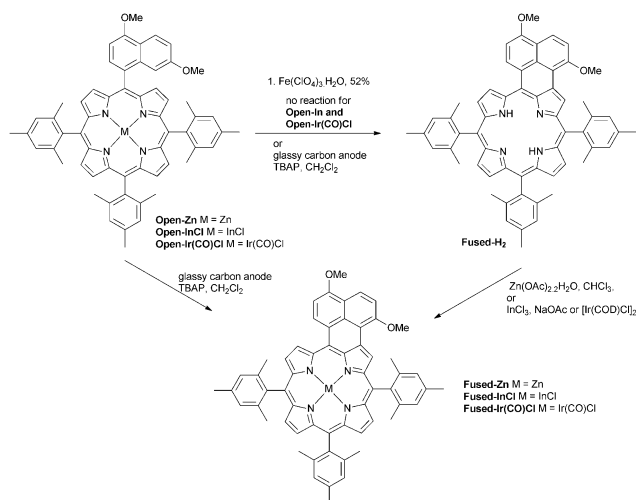
We resolved to use the same basic architecture as was shown to be successful in chemical synthesis of the same π -extended porphyrins *i.e.* porphyrins possessing three mesityl groups and one 4,7-dimethoxynaphthalen-1-yl unit.¹¹ The rationale behind this choice was the possibility to compare properties 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-H₂**, which was subsequently transformed into the zinc complex **Open-Zn**, which was then chemically oxidized with Fe(ClO₄)₃·H₂O to afford **Fused-H₂** in 52% yield.¹¹ As described previously, the Lewis acid character of Fe³⁺ causes quantitative removal of zinc during oxidative aromatic coupling. The porphyrin **Fused-H₂** 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 CH₂Cl₂ are given in Table S1 (ESI†). These tables also include

^a Department of Chemistry, University of Houston, 4800 Calhoun Road,
77204-5003, USA. E-mail: kkadish@uh.edu

^b Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52,
01-224 Warsaw, Poland. E-mail: dtgryko@icho.edu.pl

† Electronic supplementary information (ESI) available: Full synthetic and analytical data of compounds **TMP-Zn**, **TMP-InCl**, **TMP-Ir(CO)Cl**, **Open-Ir(CO)Cl**, **Open-InCl**, **Fused-H₂**, **Fused-Zn**, **Fused-InCl**, **Fused-Ir(CO)Cl** as well as copies of ¹H NMR. See DOI: 10.1039/c4cc02759k



Scheme 1 Chemical and electrochemical synthesis of π -extended porphyrins.

Table 1 Half-wave or peak potentials (V vs. SCE) in PhCN, containing 0.1 M TBAP. Scan rate of 0.1 V s⁻¹

M	Ring	Oxidation		Reduction		H-L gap (V)
		2nd	1st	1st	2nd	
H ₂	TMP	1.41	1.12	-1.19	-1.69	2.31
	Open	1.24 ^b	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 ^a	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 ^b	1.94
InCl	TMP	1.57	1.24	-1.05	-1.58	2.29
	Open	1.40 ^b	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 ^b	1.22	-1.15	-1.74	2.37
	Fused	0.85	0.53	-1.23	-1.69	1.76

^a Data taken from ref. 19. ^b Peak potential at a scan rate of 0.1 V s⁻¹.

data for the related starting compounds with a single *meso*-naphthalene group.

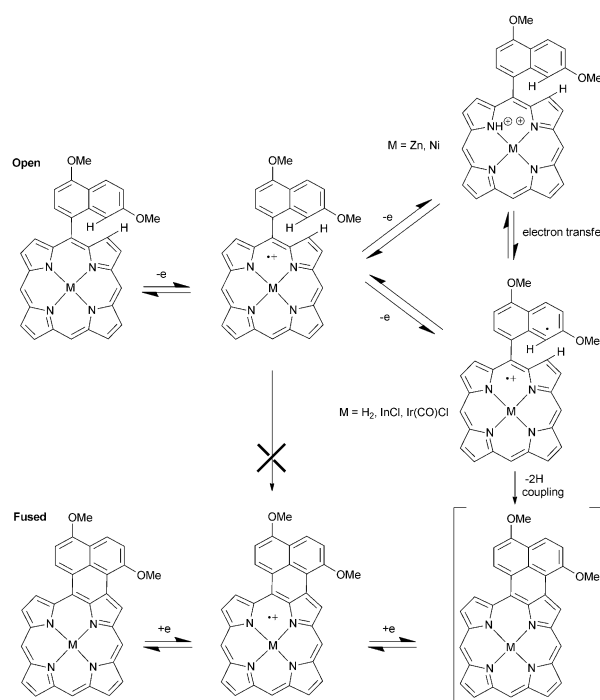
The similarity in the first reduction and first oxidation potentials of compounds having the **TMP** and **Open** macrocycles is related to the similar substituent effects of the trimesityl and naphthalene groups and to the similar sites of electron transfer, which in this case is the conjugated π -ring 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 π -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 is compared 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 conditions. 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 π -radical cation to its neutral form again. This is shown by the top cyclic voltammogram in Fig. S1a (ESI†).

The second oxidation of **Open-Zn** also occurs on the porphyrin core followed by electron-transfer leading to a 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⁻¹ 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 Fig. S1a, ESI†).

Additional evidence for electrosynthesis of the π -extended porphyrin is provided by the cyclic voltammogram in Fig. S1b (ESI†) 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 electrosynthesized **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 Fig. S1b (ESI†) with that of the chemically synthesized **Fused-Zn** in Fig. S1c (ESI†) clearly shows that the same chemical species has been formed by electrosynthesis in PhCN as that by classical chemical synthetic methods.



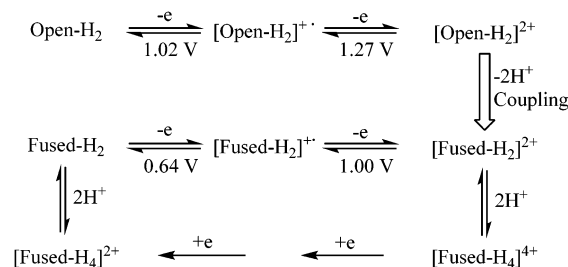
Scheme 2 Mechanism of electrochemical oxidative aromatic coupling.

In summary, electrochemical evidence suggests 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 π -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 doubly oxidized **Fused-InCl** porphyrin after controlled potential oxidation, followed by controlled potential reduction of the electrogenerated product. In this case however, after first oxidation the second one occurs on the naphthalene moiety leading directly to a bis-radical (Scheme 2).

A similar mechanism also occurs for conversion of **Open-Ir(CO)Cl** to the **Fused Ir(III)** derivatives but slight differences are seen in the UV-vis spectra of the chemically and electrochemically generated π -extended porphyrins. The chemically synthesized **Fused-Ir(CO)Cl** has a split Soret band at 463 and 493 nm and a Q band at 686 nm (see ESI† Fig. S4 and S6). Also in this case second one-electron abstractions occur at the linked naphthalene group which is electroactive and oxidized at 1.12 V in PhCN, 0.1 M TBAP.¹⁹ This difference is related to the fact that the oxidation potential of the dimethoxynaphthalenyl unit is located between the first and second oxidation potentials of the porphyrin core for **Open-In** and **Open-Ir(CO)Cl** and this is not the case for **Open-Zn**. Interestingly this difference leads to the fact that oxidative aromatic coupling occurs much easier for **Open-In** and **Open-Ir(CO)Cl** than for **Open-Zn**.

The mechanism for conversion of **Open-H₂** to **Fused-H₂** is similar to that described above for the other **Open** porphyrins but it differs from the metallated complexes in that the final electrochemically generated **Fused** product is produced as a mixture of the free-base porphyrin with an extended π ring system, **Fused-H₂**, and the diprotonated **Fused** free-base porphyrin represented as **[Fused-H₄]²⁺** (Scheme 3). Evidence for



Scheme 3 Detailed mechanism of electrochemical oxidative aromatic coupling for free-base porphyrins.

this assignment is given by cyclic voltammetry and thin-layer spectroelectrochemistry (Fig. S1–S10, ESI†). The electrochemically mediated oxidative couplings of **Open-H₂** and **Open-InCl** have been performed on the 5–10 mg scale and **Fused-H₂** and **Fused-InCl** were isolated in good yields by chromatography.

In conclusion, the use of electrochemical oxidation allows one to overcome problems with oxidative aromatic coupling of free-base porphyrins using chemical one-electron oxidants. In contrast oxidative aromatic coupling can be driven by electrochemistry giving rise directly to a fused porphyrin as a dication. Finally even indium(III) and iridium(III) porphyrins, possessing relatively high oxidation potentials, were successfully coupled to the π -extended porphyrins for the first time. The electrochemical and spectroelectrochemical data seem to demonstrate that oxidative aromatic coupling does not occur after formation of a radical-cation but only after formation of a bis-radical where the first electron is abstracted from the porphyrin π ring system and the second from the electroactive naphthalene group.

The authors thank the Robert A. Welch Foundation (K.M.K., Grant E-680) and the Foundation for Polish Science (TEAM 2009-4/3).

Notes and references

- J. L. Sessler and D. Seidel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5134.
- (a) A. M. V. M. Pereira, S. Richeter, C. Jeandon, J.-P. Gisselbrecht, J. Wytko and R. Ruppert, *J. Porphyrins Phthalocyanines*, 2012, **16**, 464; (b) D. Kim and A. Osuka, *Acc. Chem. Res.*, 2004, **37**, 735; (c) A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79.
- A. Nowak-Król and D. T. Gryko, *Org. Lett.*, 2013, **15**, 5618.
- V. V. Diev, K. Hanson, J. D. Zimmerman, S. R. Forrest and M. E. Thompson, *Angew. Chem., Int. Ed.*, 2010, **49**, 5523.
- H. Yamada, D. Kuzuhara, T. Takahashi, Y. Shimizu, K. Uota, T. Okujima, H. Uno and N. Ono, *Org. Lett.*, 2008, **10**, 2947–2950.
- N. K. S. Davis, M. Pawlicki and H. L. Anderson, *Org. Lett.*, 2008, **10**, 3945.
- Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 4119.
- Z. S. Yoon, J. H. Kwon, M.-C. Yoon, M. K. Koh, S. B. Noh, J. L. Sessler, J. T. Lee, D. Seidel, A. Aguilar, S. Shimizu, M. Suzuki, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2006, **128**, 14128.
- (a) D. A. Whiting, *Comprehensive Organic Synthesis*, 1991, vol. 3, p. 659; (b) M. Grzybowski, K. Skonieczny, H. Butenschön and D. T. Gryko, *Angew. Chem., Int. Ed.*, 2013, **52**, 9900.
- H. Mori, T. Tanaka and A. Osuka, *J. Mater. Chem. C*, 2013, **1**, 2500.
- J. P. Lewtak, D. Gryko, D. Bao, E. Sebai, O. Vakuliuk, M. Ścigaj and D. T. Gryko, *Org. Biomol. Chem.*, 2011, **9**, 8178.
- T. Tanaka, N. Aratani, J. M. Lim, K. S. Kim, D. Kim and A. Osuka, *Chem. Sci.*, 2011, **2**, 1414.

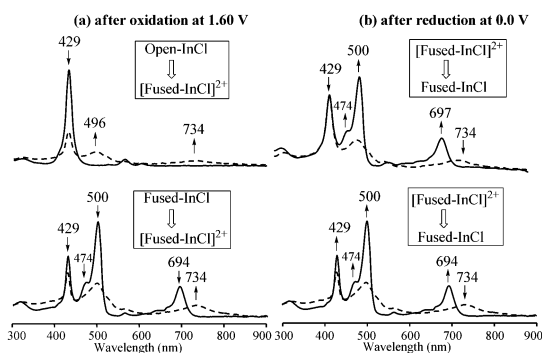


Fig. 1 UV-visible spectrum of **Open-InCl** and **Fused-InCl** in PhCN, 0.1 M TBAP (a) after a two electron oxidation and (b) after a two electron reduction of the doubly oxidized species.

- 13 T. K. Ahn, K. S. Kim, D. Y. Kim, S. B. Noh, N. Aratani, C. Ikeda, A. Osuka and D. Kim, *J. Am. Chem. Soc.*, 2006, **128**, 1700.
- 14 C. Jiao, K.-W. Huang and J. Wu, *Org. Lett.*, 2011, **13**, 632.
- 15 K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem.*, 2006, **118**, 4048; K. Kurotobi, K. S. Kim, S. B. Noh, D. Kim and A. Osuka, *Angew. Chem., Int. Ed.*, 2006, **45**, 3944.
- 16 H. Schäfer, Electrolytic oxidative coupling, in *Organic Electrochemistry*, ed. H. Lund and O. Hammerich, Marcel Dekker, New York, 4th edn, 2001, p. 883.
- 17 A. Kirste, B. Elser, G. Schnakenburg, F. Stecker and S. R. Waldvogel, *J. Am. Chem. Soc.*, 2012, **134**, 3571.
- 18 (a) M. Buda, A. Iordache, C. Bucher, J.-C. Moutet, G. Royal, E. Saint-Aman and J. L. Sessler, *Chem. – Eur. J.*, 2010, **16**, 6810; (b) T.-T. Bui, A. Iordache, Z. Chen, V. V. Roznyatovskiy, E. Saint-Aman, J. M. Lim, B. S. Lee, S. Ghosh, J.-C. Moutet, J. L. Sessler, D. Kim and C. Bucher, *Chem. – Eur. J.*, 2012, **18**, 5853.
- 19 P. Chen, Y. Fang, K. M. Kadish, J. P. Lewtak, D. Koszelewski, A. Janiga and D. T. Gryko, *Inorg. Chem.*, 2013, **52**, 9532.