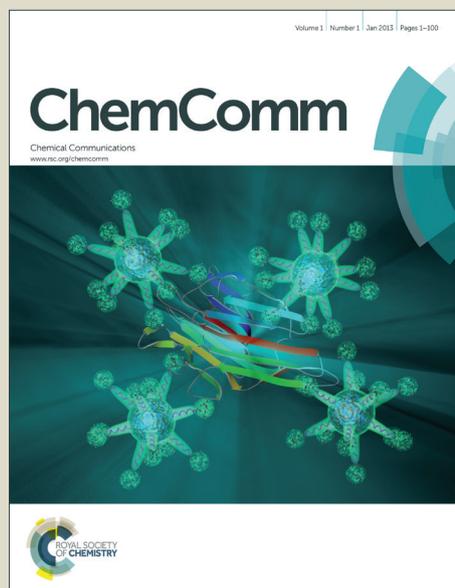


ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Reductive Electropolymerization of *N*-methyl-3-pyridylethynyl-porphyrins

Sung-Chou Huang, and Ching-Yao Lin*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Cyclic voltammograms, UV-visible and FT-IR spectra show that porphyrins with two *N*-methyl-3-pyridylethynyl substituents can undergo reductive electropolymerization onto Pt and ITO electrodes. The films are redox active and a mechanism is suggested.

Porphyrin electropolymerized films exhibit rich electron-transfer chemistry and they are good candidates for a variety of important applications, such as solar energy conversion,¹ catalysis,² fuel cell³ and sensor^{1a,4,5a} studies. Porphyrin electropolymerized films used in the above-mentioned applications were mostly generated by oxidizing monomeric porphyrins in solutions.⁵ It is extremely rare to polymerize porphyrins onto electrodes by reductions. In this report, we demonstrate that reductive electropolymerization can be carried out by reducing porphyrins with *N*-methyl-3-pyridylethynyl substituents. To the best of our knowledge, this may be the first example to observe such a phenomenon of porphyrins.

We have previously reported series of electron-deficient porphyrins.⁶ Fig. 1 collects (a) the chemical structures of selected zinc porphyrins (denoted as Zn2, Zn4, and Zn6) and (b) their cyclic voltammograms (CV). It has been established that the first two reductions of Zn2 and Zn6 are *quasi*-reversible, one-step one-electron reductions at around -0.60 V vs. SCE.^{6a} In sharp contrast, the reductions of Zn4 show two irreversible waves peaked at -0.75 and -0.98 V vs. SCE. It is logical to suggest that the differences in reversibility of the CVs should be related to the differences in the chemical structures (*vide infra*). We recently discovered that, upon repeated scans, these irreversible waves rapidly intensified and transformed into a reversible redox couple at -1.38 V vs. SCE (Fig. 2a). These behaviours are consistent with the formation of an electropolymerized film onto a working electrode.^{5c} After electropolymerization, the Pt working electrode was taken out of the porphyrin solutions, rinsed with DMF to remove loosely attached porphyrin molecules on the surface of the Pt electrode, and dried in air. The electrode was then put into a blank solution (DMF with 0.1M TBAP, no porphyrins) for further examination. Fig. 2b shows the electrochemical responses of such an electrode in the blank solution. As shown in the figure, the redox couple was stabilized after 20 repeated scans. The remaining signals suggest that the newly formed substance on the electrode is stable in the solution and it is electrochemically active.

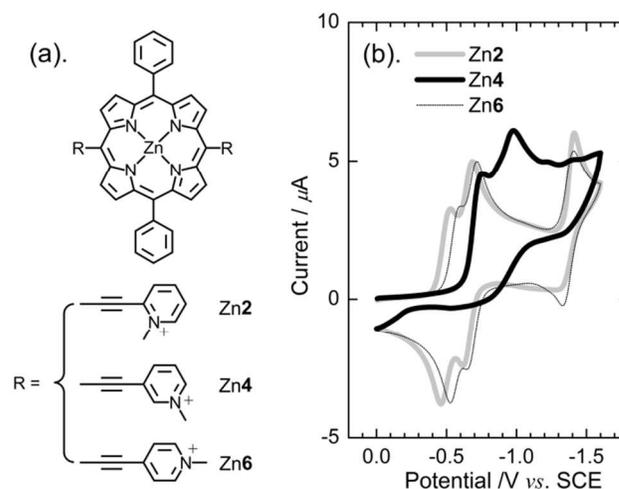


Fig. 1 (a) Structural diagram of 10,20-bis-(*N*-methyl-2, 3, or 4-pyridylethynyl)-5,15-biphenylporphinato zinc(II), denoted as Zn2, Zn4, and Zn6, respectively. (b) CVs of Zn2 (grey), Zn4 (bold black), and Zn6 (thin black) in DMF/0.1M TBAP. Experimental conditions: 1 mM of the porphyrins, Pt working and counter electrodes, SCE reference electrode and the scan rate = 100 mV/s.

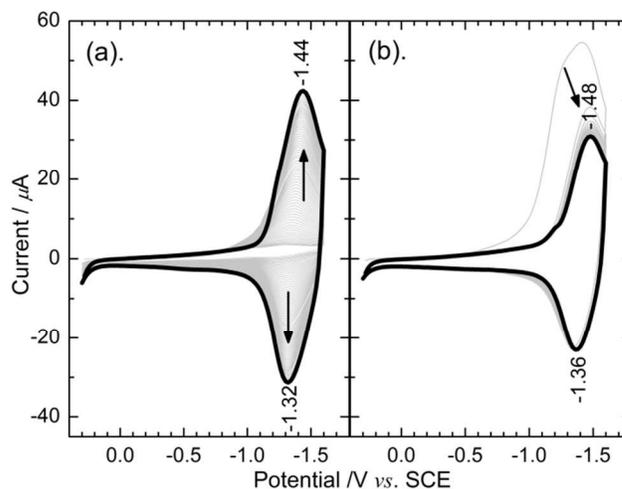


Fig. 2 (a) CV of Zn4 upon 70 repeated scans in DMF/0.1M TBAP. The bold solid line represents the final scan. Experimental conditions: 0.2 mM of Zn4, Pt working and counter electrodes, SCE reference electrode and the scan rate = 100 mV/s. (b) Stabilization of Zn4-modified Pt electrode by 20 repeated scans (scan rate = 100 mV/s) in the blank solution. The bold solid line represents the final scan.

To further study the properties of the porphyrin films, Zn4 was electropolymerized onto ITO plates for the UV-visible and FT-IR spectra. The photos of the ITO plates are put in Fig. S1 (ESI). For UV-visible absorption, a thin and transparent film was generated by 10 scans in the porphyrin solution followed by rinsing with DMF, drying in air, and then used directly for UV-visible measurement. For FT-IR, a thicker film was produced by 70 scans in the porphyrin solution followed by rinsing with DMF. The air-dried film was scraped off the ITO plate and mixed with KBr to make a pellet for the FT-IR measurement. The spectra are shown in Fig. 3. For the UV-visible spectra, both the film and the molecular sample in DMF exhibit typical porphyrin features, strong B bands in the 450-nm region and weaker Q bands at ~660 nm. The absorption bands of the film, however, are broadened and slightly blue-shifted from those of the solution sample. These differences might reflect intermolecular interactions between the molecules in the films. Nonetheless, the similarity between the film and the solution spectra strongly suggests that the pi-conjugation system of Zn4 is intact upon electropolymerization. For the FT-IR (Fig. 3b), the film sample also shows broadened spectra. Importantly, stretching modes of the ethynyl groups can be found at 2192 and 2189 cm⁻¹ for the molecular and the film samples, respectively. This suggests that the ethynyl groups of Zn4 are not affected upon electropolymerization. In other words, Fig. 3 suggests that the electropolymerization reactions may take place at the pyridinium rings.

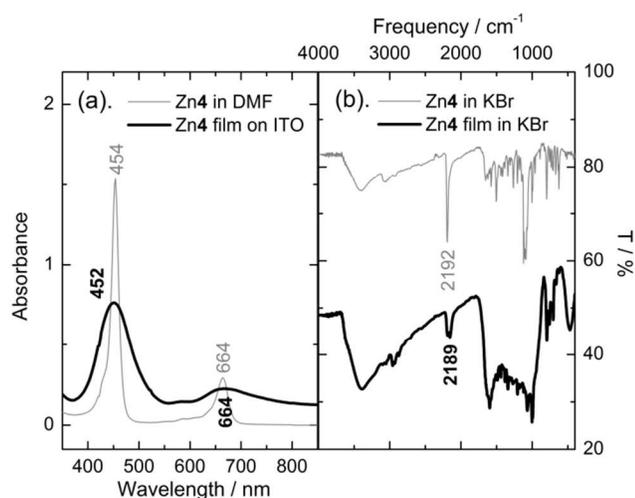


Fig. 3 (a). UV-visible spectra of Zn4 in DMF and Zn4 film on ITO. (b). FT-IR of Zn4/KBr and Zn4 film/KBr.

Regarding the mechanism, we adopt the model suggested by Birss and co-workers for reductive deposition of quaternary pyridinium onto glassy carbon electrodes.⁸ According to their report, a reduced quaternary pyridinium ring would polymerize with other reduced quaternary pyridinium rings at the *para*-positions. Based on that model, Fig. 4 depicts a reductive electropolymerization mechanism of Zn4. As shown in the figure, Zn4 first receives two electrons and the electrons remain at the pyridinium rings because the chemical structure of Zn4 prevents delocalization of the electrons. Following the electrochemical step, the doubly reduced Zn4 could undergo dimerization or polymerization reactions at the pyridinium rings, *i.e.* an EC mechanism.⁹ The proposed mechanism is consistent with the

experimental findings. First of all, this mechanism suggests that Zn4 receives two electrons per molecule as in the case of Zn2 and Zn6. Secondly, the two added electrons of Zn4 dianion are localized at the pyridinium rings whereas the electron density of doubly reduced Zn2 and Zn6 can be delocalized to the porphyrin core *via* the ethynyl bridges. This is consistent with Zn2 and Zn6 dianions being much more stable than Zn4 dianion, resulting in reversible CVs of Zn2 and Zn6 and irreversible CV of Zn4 (Fig. 1b). Thirdly, the UV-visible and FT-IR spectra suggest minimal impact to the chemical structures of the porphyrin core as well as the ethynyl bridges upon polymerization. This is consistent with the suggestion that the polymerization process may occur at the pyridinium rings.

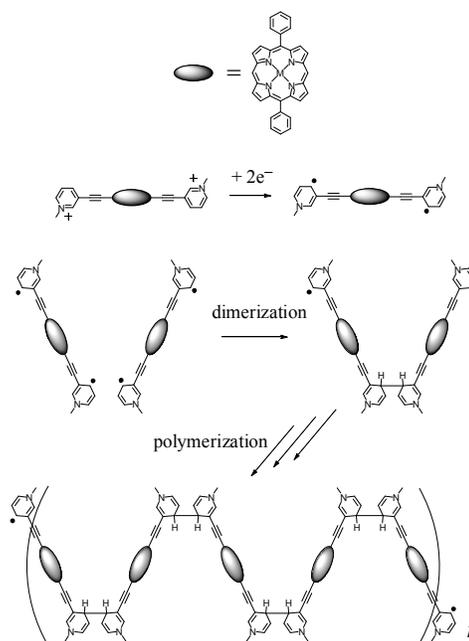


Fig. 4 Proposed mechanism of Zn4 reductive electropolymerization.

In order to visualize possible spatial arrangements of the porphyrins within the polymers, we carried out geometry optimization of Zn4 pentamer (Fig. S2, ESI). Two arrangements were calculated: Two protons of the linked pyridinium rings are at *syn*- or *anti*-conformation. In both cases, the results suggest limited interactions between/among the porphyrins within the same polymer strain. This is consistent with similar UV-visible spectra of the molecular and the film samples in Fig. 3a. Finally, the reductive electropolymerization is not limited to Zn4. H₂4, Ni4, and Mn4 can also undergo such reactions (Fig. S3, S4, and S5, ESI). This implies that future applications in sensors and catalysis may be possible.

Conclusions

In this study, we report possibly the first example of reductive electropolymerization for porphyrins. The electropolymerized films are redox active and their formation is not very sensitive to porphyrin central metals. More studies regarding how the electropolymerization procedures (scan rates, thickness, *etc.*) would affect the properties and the applications of the films are underway.

Acknowledgment

This work is supported by the Ministry of Science and Technology, Taiwan.

Notes and references

- ⁵ Department of Applied Chemistry, National Chi Nan University. 302 University Road, Puli, Nantou Hsien 54561, Taiwan. Fax: +886-49-2917956; Tel: +886-49-2910960 ext. 4152. Email: cyl@ncnu.edu.tw
- † Electronic Supplementary Information (ESI) available: [Photos of ITO electrodes, Optimized geometry diagram of Zn₄ pentamers, structural diagrams and electrochemistry and electropolymerization data of H₂, Ni₄, and Mn₄]. See DOI: 10.1039/b000000x/
- (a) B. J. Brennan, P. A. Liddell, T. A. Moore, A. L. Moore, D. Gust, *J. Phys. Chem. B* 2013, **117**, 426-432. (b) M. G. Walter, C. C. Wamser, *J. Phys. Chem. C* 2010, **114**, 7563-7574. (c) J. Chen, D. L. Officer, J. M. Pringle, D. R. MacFarlane, C. O. Too, G. G. Wallace, *Electrochem. Solid-State Lett.* 2005, **8**, A528-A530. (d) H. Winnischofer, A. L. B. Formiga, M. Nakamura, H. E. Toma, K. Araki, A. F. Nogueira, *Photochem. Photobiol. Sci.*, 2005, **4**, 359-366.
 - (a) C. Poriel, Y. Ferrand, P. le Maux, C. Paul, J. Rault-Berthelot, G. Simonneaux, *Chem. Commun.*, 2003, 2308-2309. (b) S. Griveau, F. Bedioui, *Electroanalysis*, 2001, **13**, 253-256. (c) M. Lucero, G. Ramirez, A. Riquelme, I. Azocar, M. Isaacs, F. Armijo, J. E. Forster, E. Trollund, M. J. Aguirre, D. Lexa, *J. Mol. Catal. A: Chem.*, 2004, **221**, 71-76. (d) F. Bedioui, J. Devynck, C. Bied-Charreton, *J. Mol. Catal. A: Chem.*, 1996, **113**, 3-11.
 - (a) A. Bettelheim, L. Soifer, E. Korin, *J. Power Sources*, 2004, **130**, 158-162. (b) A. Bettelheim, L. Soifer, E. Korin, *J. Electroanal. Chem.*, 2004, **571**, 265-272.
 - (a) R. Matsuoka, M. Igarashi, T. Kondo, T. Aikawa, M. Yuasa, *J. Electrochem. Soc.*, 2014, **161**, B163-B166. (b) B. J. Brennan, P. A. Liddell, T. A. Moore, Ana L. Moore, D. Gust, *J. Phys. Chem. B*, 2013, **117**, 426-432. (c) L. Lvova, M. Mastroianni, C. Di Natale, I. Lundstroem, R. Paolesse, *Electroanalysis*, 2012, **24**, 776-789.
 - For reviews: (a) P. S. Sharma, A. Pietrzyk-Le, F. D'Souza, W. Kutner, *Anal. Bioanal. Chem.*, 2012, **402**, 3177-3204. (b) M. G. Walter, A. B. Rudine, C. C. Wamser, *J. Porphyrins Phthalocyanines*, 2010, **14**, 759-792. (c) N. M. Boyle, J. Rochford, M. T. Pryce, *Coord. Chem. Rev.*, 2010, **254**, 77-102. (d) F. Bedioui, J. Devynck, C. Bied-Charreton, *J. Mole. Catal. A: Chem.*, 1996, **113**, 3-11. (e) F. Bedioui, J. Devynck, *Acc. Chem. Res.* 1995, **28**, 30-36.
 - (a) C.-Y. Lin, L.-C. Chuang, Y.-F. Yang, C.-L. Lin, H.-C. Kao, W.-J. Wang, *Dalton Trans*, 2004, 456-462 (b) C.-Y. Lin, L.-C. Chuang, Y.-C. Lin, C.-L. Lin, *Dalton Trans.*, 2004, 4006-4009. (c) C.-Y. Lin, Y.-C. Chen, C.-W. Yao, S.-C. Huang, Y.-H. Cheng, *Dalton Trans.*, 2008, 793-799.
 - M. J. Gouterman, *Mol. Spectrosc.*, 1961, **6**, 138-163.
 - R. P. C. Wong, J. E. Wong, V. I. Birss, *Can J. Chem.*, 2004, **82**, 1536-1544.
 - A. J. Bard and L. R. Faulkner, in *Electrochemical Methods: Fundamentals and Applications* 2nd Ed., John Wiley & Sons, Inc., New York, 2001, pp. 473-474.