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Electronic Supplementary Information to

Reductive Electropolymerization of *N*-methyl-3-pyridylethynylporphyrins

Sung-Chou Huang, and Ching-Yao Lin*

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

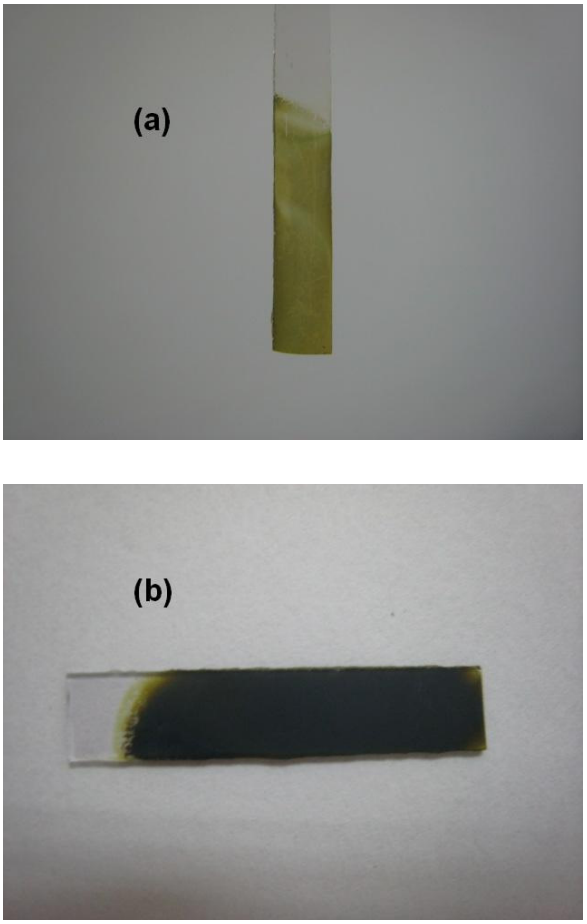
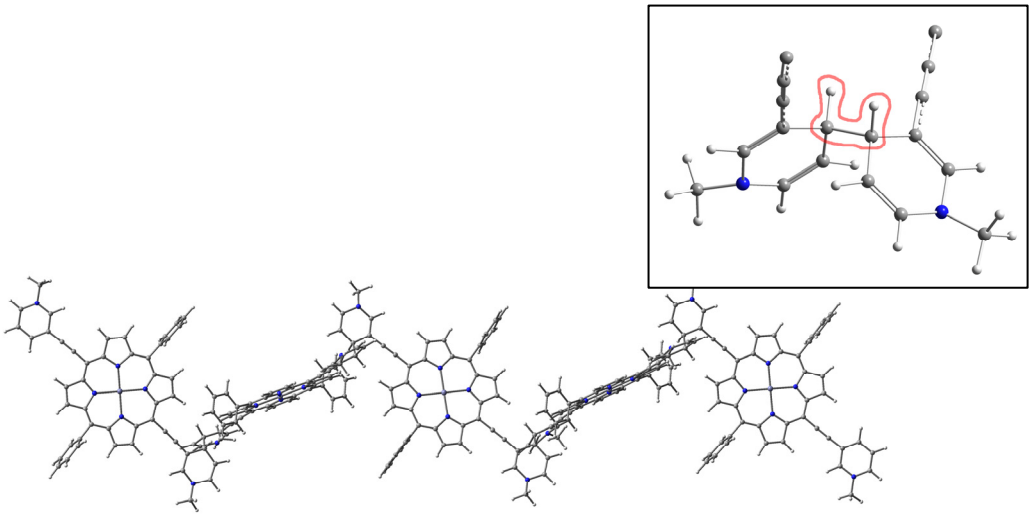


Fig. S1. Electropolymerized films of Zn 4 on ITO electrodes (a) after 10 repeated scans and (b) after 70 scans. Electropolymerization conditions: 0.2 mM of Zn**4** in DMF/0.1M TBAP under N_2, Pt working and counter electrodes, SCE reference electrode and the scan rate = 100 mV/s.

(a) *syn*



(b) *anti*

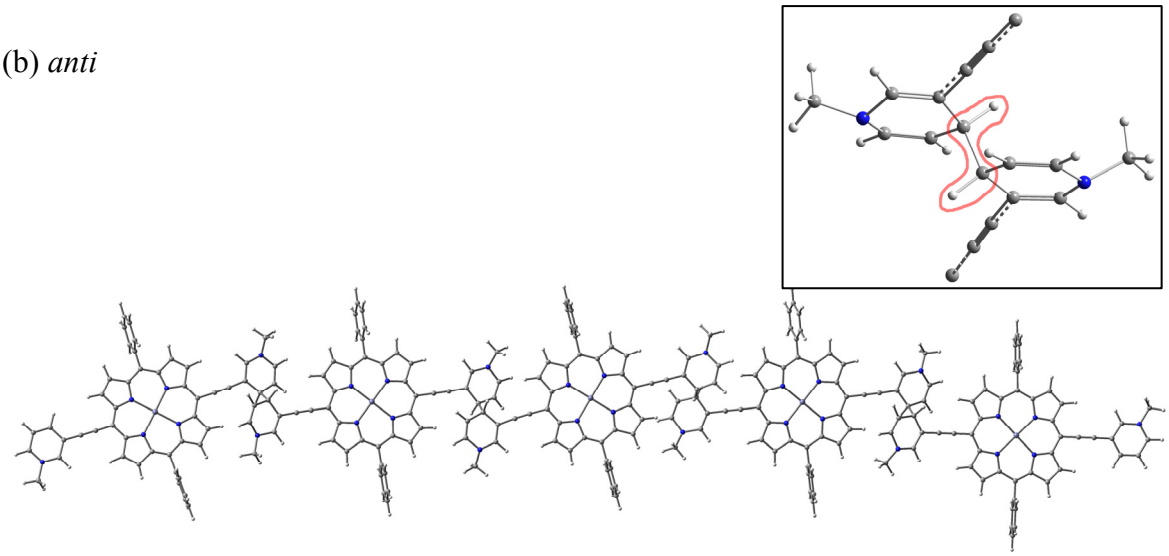


Fig. S2. Optimized geometry diagrams of Zn**4** pentamers (MOPAC, PM3). The two protons of the linked pyridinium rings are at (a) *syn*- and (b) *anti*-conformation. Insets: chemical structures around the linked pyridinium rings. Both conformations suggest limited interactions between/among the porphyrins within the same polymer strain.

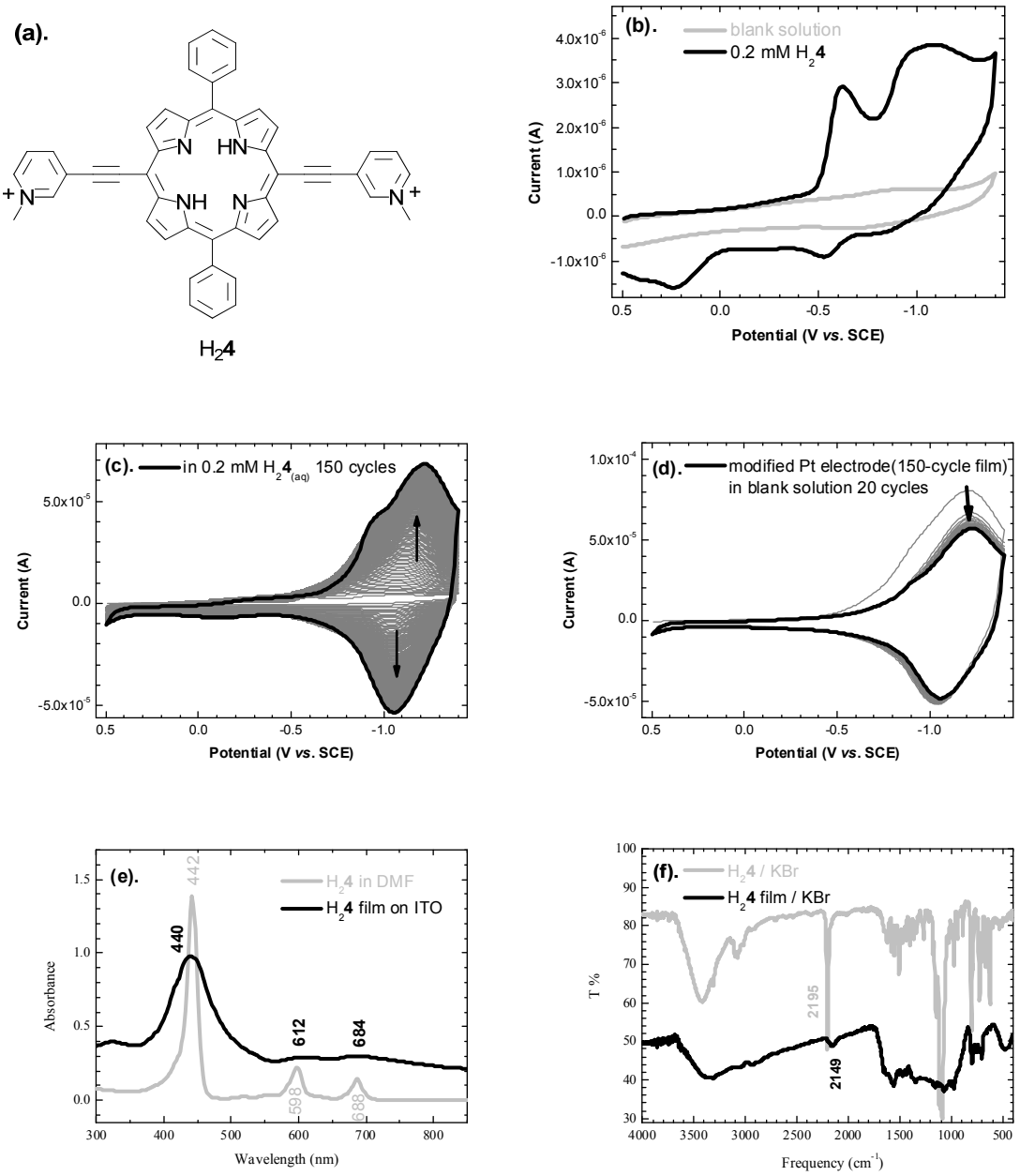


Fig. S3. (a) Chemical structure of H_2**4**, (b) CV of H_2**4**, (c) electropolymerization of H_2**4**, (d) stabilization of H_2**4**-modified Pt electrode in the blank solution, (e) UV-visible spectra of H_2**4** molecules in DMF (grey) and film on ITO (black), and (f) FT-IR spectra of H_2**4** molecules (grey) and film (black). Electrochemistry conditions: 0.2 mM H_2**4** in DMF/0.1M TBAP under N_2, Pt working and counter electrodes, SCE reference electrode, scan rate = 100 mV/s.

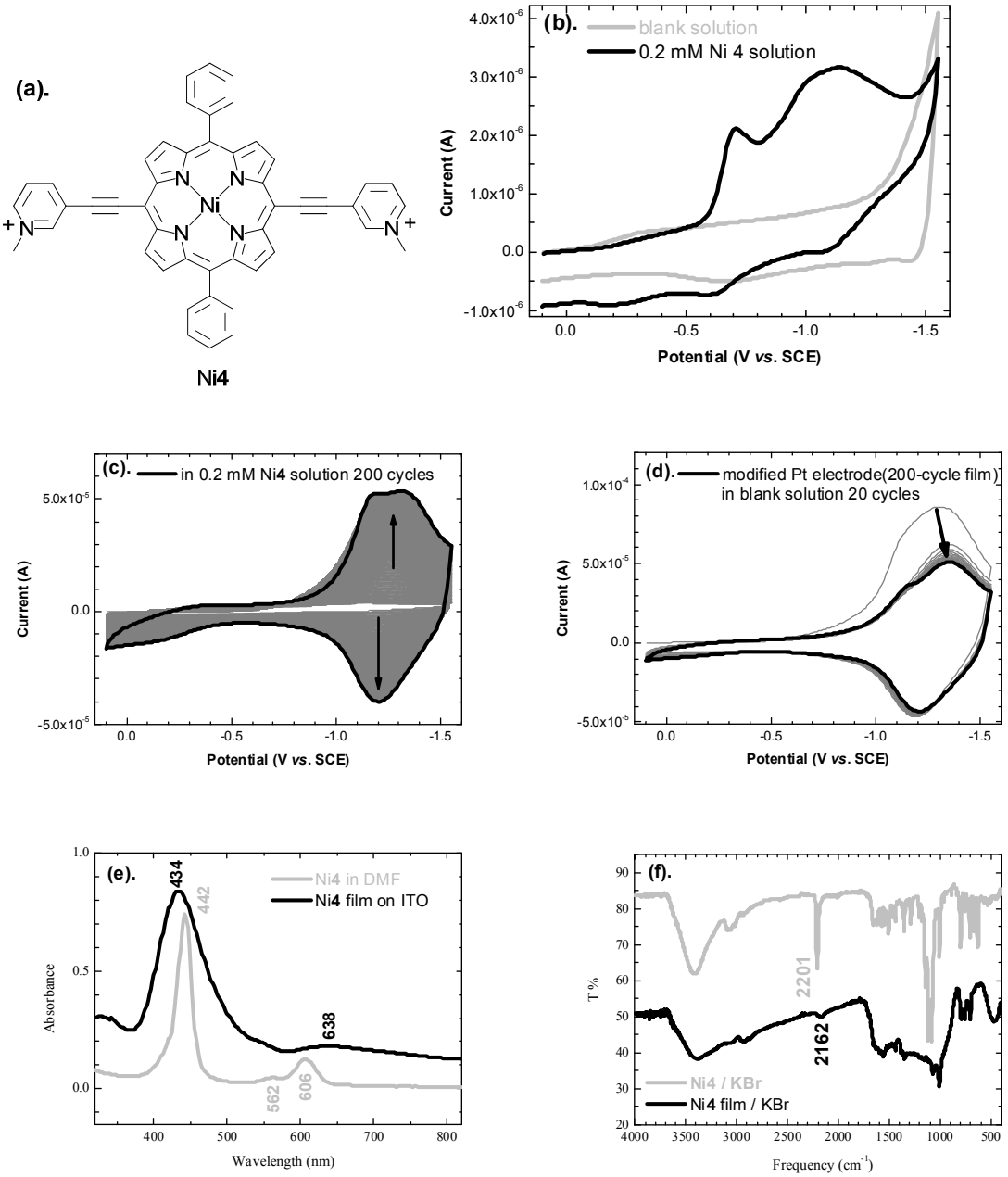


Fig. S4. (a) Chemical structure of Ni**4**, (b) CV of Mn4, (c) electropolymerization of Ni**4**, (d) stabilization of Ni**4**-modified Pt electrode in the blank solution, (e) UV-visible spectra of Ni**4** molecules in DMF (grey) and film on ITO (black), and (f) FT-IR spectra of Ni**4** molecular (grey) and film (black). Electrochemistry conditions: 0.2 mM Ni**4** in 0.1M TBAP/DMF, Pt working and counter electrodes, SCE reference electrode, scan rate = 100 mV/s.

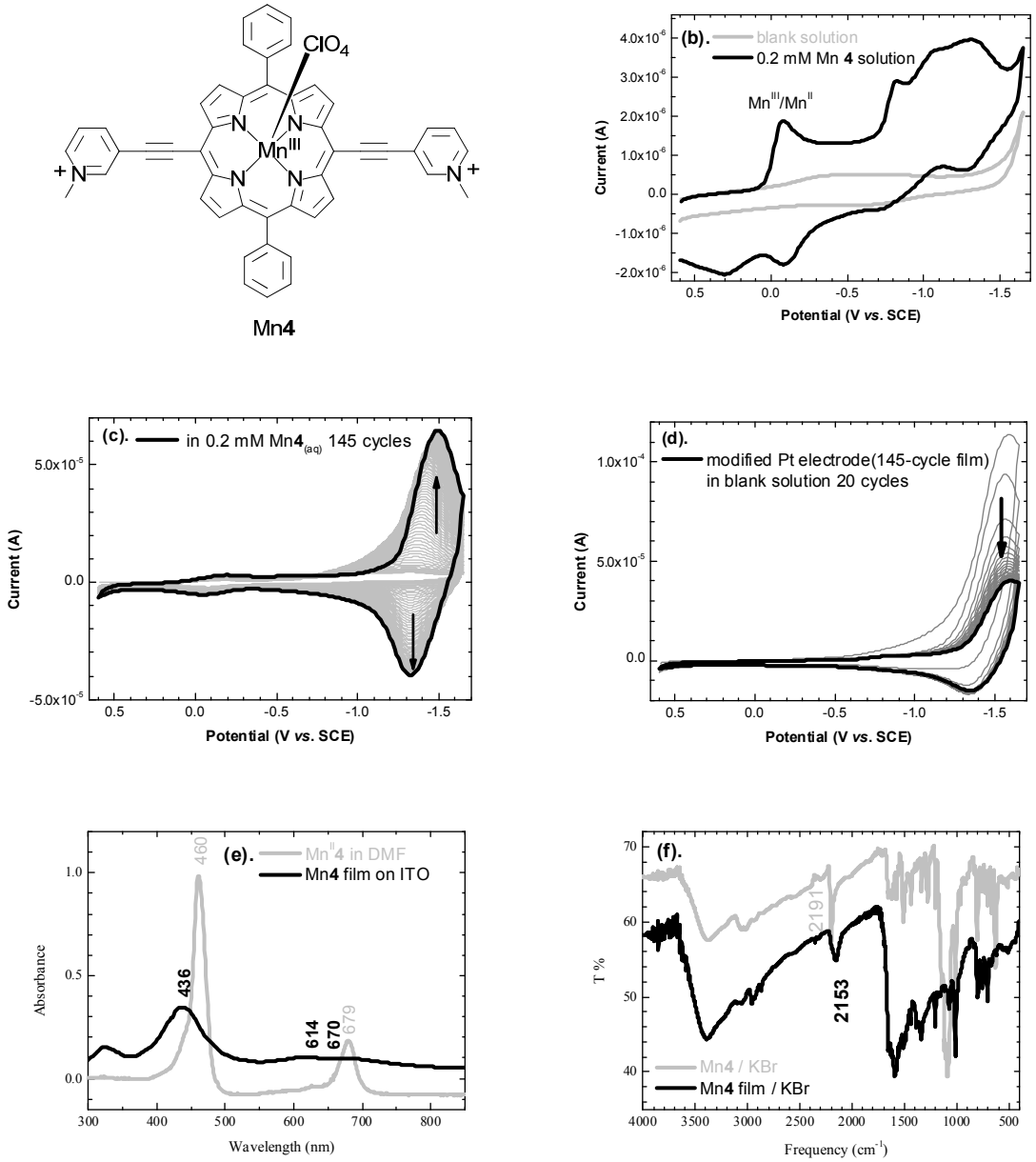


Fig. S5. (a) Chemical structure of Mn**4**, (b) CV of Mn**4**, (c) electropolymerization of Mn**4**, (d) stabilization of Mn**4**-modified Pt electrode in the blank solution, (e) UV-visible spectra of Mn**4** molecules in DMF (grey) and film on ITO (black), and (f) FT-IR spectra of Mn**4** molecules (grey) and film (black). Electrochemistry conditions: 0.2 mM Mn**4** in DMF/0.1M TBAP under N_2, Pt working and counter electrodes, SCE reference electrode, scan rate = 100 mV/s.