Supplementary Material (ESI) for Chemical Communications

Title: Electrochemically Controlled Ligand Shuttling between Zinc Porphyrin and *meso*-Phenylenediamine Substituent

Authors: Kuo Yuan Chiu[a] and Yuhlong Oliver Su*[a,b]
[a] Department of Applied Chemistry, National Chi Nan University
1, University Road, Puli, Nantou Hsien, Taiwan 545 Fax:
886-49-2917956; Tel: 886-49-2910960 ext.4150;
[b] Department of Chemistry, National Chung Hsing University, 250, Kuo Kuang Rd., Taichung, Taiwan 402 Tel: 886-4-22840537

Supporting information

1. Experimental section
2. Electrochemical studies
3. Spectroelectrochemical studies
4. Scheme S1-S4; Figure S1-S9.

Supplementary information

Experimental section

The starting chemicals for porphyrin synthesis were obtained commercially. Pyrrole, mesitylaldehye and 4-nitrobenzaldehyde were obtained from ACROS. (Organic solvents were degassed by purging with pre-purified nitrogen gas and dried before use.[S1]) Analytical grade tetra-*n*-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried *in vacuo* prior to use.

Electrochemistry was performed with a CHI Model 760 series electroanalytical workstation. Cyclic voltammetry was conducted with the use of a three-electrode cell in which a BAS glassy carbon electrode (area = 0.07 cm^2) was used as working electrode. The glassy carbon electrode was polished with 0.05 μm alumina on Buehler felt pads and was ultrasonicated for 1 min to remove the alumina residue. The auxiliary electrode is a platinum wire and the reference electrode is a home-made Ag/AgCl, KCl(sat.) reference electrode, which is separated from the test solution by a porous glass frit. The spectroelectrochemical cell was composed of a 1 mm cuvette, a reticulated vitreous carbon or platinum gauze thin layer as working electrode, a platinum wire as auxiliary electrode, and an Ag/AgCl, KCl(sat.) reference electrode. Absorption spectra were measured with a HP-8453 UV/vis spectrophotometer. ^1H NMR spectra were obtained with a Varian Unity Inova 300 WB spectrometer. EPR spectra were measured with a Bruker Model EMX-10/12 spectrometer.

The structure of ZnTMP-PD and its synthesis pathway are shown in scheme S1.

Compound **1** was prepared following Lindsey's methods.[S2] Yield : 6 %. UV/Vis(CH_2Cl_2)λ_{max}/nm : 419, 516, 550, 592, 648 ; MS (FAB^+) : *m/z* 786.4 ($[M+H]^+$) ; ^1H NMR($CDCl_3$/ppm) : δ 8.727 (2H, d), 8.669 (2H, d), 8.653 (4H, s), 8.623 (2H, d), 8.387 (2H, d), 7.285 (6H, s), 2.630 (9H, s), 1.853 (18H, d), -2.565 (2H, s).

Compound **2** was obtained by the reduction of the corresponding nitro porphyrin.[S3] Yield : 65 %. UV/Vis(CH_2Cl_2)λ_{max}/nm : 421, 517, 552, 592, 650 ; MS (FAB$^+$) : *m*/*z* 756.4 ($[M+H]^+$) ; ^1H NMR($CDCl_3$/ppm) : δ 8.871 (2H, d), 8.669 (2H, d), 8.622 (4H, s), 7.979 (2H, d), 7.280 (6H, s), 7.054 (2H, d), 5.304 (2H, s), 2.631 (9H, s), 1.857 (18H, d), -2.539 (2H, s).

Compound **3** was obtained by metallation of the free base porphyrin (compound **2**) with excess zinc acetate (in methanol) under nitrogen in CH_2Cl_2 for 2 h at room temperature. Completion of the reaction was checked by the shift of the Q bands spectrophotometrically. The solution was evaporated and further purified by column chromatography on silica gel with CH_2Cl_2. Yield : 88 %. UV/Vis(CH_2Cl_2)λ_{max}/nm : 308, 422, 551, 592 ; MS (FAB$^+$) : *m*/*z* 817.3 (M^+) ; ^1H NMR($CDCl_3$/ppm) : δ 8.816 (2H, d), 8.716 (2H, d), 8.686 (4H, s), 7.779 (2H, d), 7.260 (6H, s), 6.355 (2H, d), 5.299 (2H, s), 2.625 (9H, s), 1.850 (18H, d).

ZnTMP-PD synthesis : A stirred solution of TPA-Br (11 mg, 0.034 mmol), compound **3** (25.7 mg, 0.034 mmol), $Pd_2(dba)_3$ (1 mg, 0.01 mmol), dppf (1 mg, 0.01 mmol), and Na^{t}OBu (3.26 mg, 0.034 mmol) in toluene (10 mL) was heated at reflux under N_2 atmosphere for 48 h. The filtrate was collected and evaporated under vacuum. The crude product was purified by chromatography on silica gel, using dichloromethane/hexane (1:1) as the eluent to give ZnTMP-PD as a purple-red solid (10 mg). Yield : 27.8 %. UV/Vis(CH_2Cl_2)λ_{max}/nm : 308, 421, 550 , 593 ; MS (FAB$^+$) : *m*/*z* 1061.4253 (M^+) ; FT-IR(KBr, cm^{-1}) : 3409, 1594, 1461, 1384, 997 ; ^1H NMR($CDCl_3$/ppm) : δ 8.988 (2H, d), 8.784 (2H, d), 8.706 (4H, s), 8.108 (2H, d), 7.419

(2H, d), 7.287 (14H, m), 7.176 (4H, t), 7.076 (2H, t), 1.149 (27H, s).

Elecrtrochemical studies

ZnTMP had two reversible redox couples in oxidation,[S4] $E_{1/2}$ =+0.79 and +1.11V, respectively (figure S3). When 0.5 equivalent of MeIm (*N*-methylimidazole) was added to the solution, (MeIm)ZnTMP was formed. The new complex was easier to be oxidized than ZnTMP for the first oxidation, but its second oxidation was harder.[S4] The first redox couple of ZnTMP gradually decreased and a new wave before the first oxidation wave appeared (scheme S4). Also, another new oxidation wave appeared following the second oxidation. At this equivalent, four redox couples (figure S3B) were observed. When MeIm concentration reached 1.0 equivalent, the original two redox couples completely disappeared with ΔE_{pa}'s being -0.12 and +0.21 V, respectively.

Figure S1A shows the cyclic voltammogram of ZnTMP-PD in CH_2Cl_2. In the reduction part, a reversible redox couple could be observed at $E_{1/2}$ = -1.44 V, and is attributed to the reduction on metalloporphyrin ring.

The integration areas of DPV peaks (figure S1B) were 6.93×10^{-7}, 6.89×10^{-7} and 1.42×10^{-6} VA, respectively. The third oxidation potential of ZnTMP-PD at +1.13 V is more positive than those of the second redox couples of the PD and ZnTMP (+1.01V and +1.11V, respectively). Because prior to reaching +1.00 V, the entire ZnTMP-PD had already lost two electrons, the third oxidation wave thus involves the oxidation of both moieties.

Figure S4 shows the cyclic voltammogram of *N*-methylimidazole (MeIm) with different concentration in CH_2Cl_2. In the oxidation part, no oxidation peak could be observed.

Spectroelectrochemical studies

Figure S5A shows the absorption spectra of one-electron oxidation of PD at the range of $E_{appl.}$ = +0.00 - +0.68 V. As the potential shifted positively, it was observed that the 310 nm peak of neutral PD gradually decreased in absorbance. At the same time, new absorption peaks at 397 and 787 nm gradually grew. The absorption at 787 nm was an intervalence charge-transfer (IV-CT) band.[S5, S6]

The absorption spectral change of PD in the presence of 0.75 equivalent MeIm was obtained (S5B) in comparison with figure S5A for the absorbance of IV-CT band. After PD was oxidized, MeIm formed hydrogen bonding with $PD^{+\bullet}$ to stabilize cation radicals and thus the charge transfer band decreased in absorbance.

At $E_{appl.}$ = +0.00 - +0.93 V, the spectrum of ZnTMP under each potential was obtained (figure S6A).[8b] As the potential shifted anodically, it was observed that the Soret band (420 nm) and the Q band (550 nm) absorbances gradually decreased. A small peak grew upwards at 374 nm. There was a broad band in the range of 600~800 nm, indicating the formation of the zinc porphyrin cation radical.[S4]

When 0.75 equivalent of MeIm was added to ZnTMP, there appeared a new Soret band at 430 nm, which was due to (MeIm)ZnTMP formation. At $E_{appl.}$ = +0.00 - +0.93 V, the spectrum under each potential was obtained. As the potential shifted positively, the 420 nm, 430 nm and Q band (550 nm) gradually decreased. Two new bands at 373 and 414 nm grew up. And there was a relatively broad absorption band at 600~800 nm growing (figure S6B).

References of supplementary information

S1 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Pergamon, Purification of Laboratory Chemicals, ed. Oxford, 1980.

S2 J. S. Lindsey and W. Wagner, *J. Org. Chem.*, 1989, **54**, 828.

S3 Y. Sun, A. E. Martell and M. Tsutsui, *J. Heterocycl. Chem.*, 1986, **23**, 561.

S4 C. –L. Lin, M. –Y, Fang and S. –H. Cheng, *J. Electroanal. Chem.* 2002, **531**, 155.

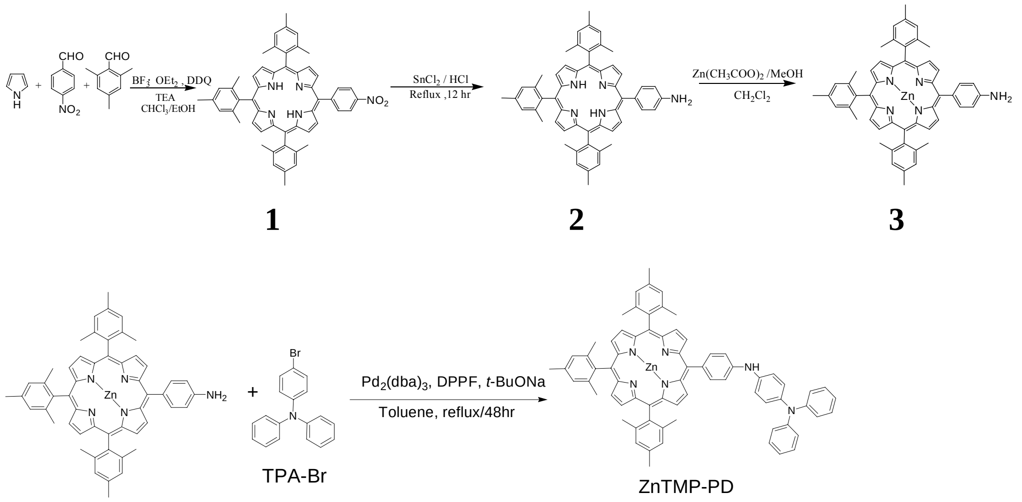
S5 C. Lambert and G. Noll, *J. Am. Chem. Soc.* 1999, **121**, 8434.

S6 S. J. Yeh, C. Y. Tsai, C. Y. Huang, G.-S. Liou and S.-H. Cheng, *Electrochem. Commun.* 2003, **5**, 373.

S7 Y. Hirao, A. Ito and K. Tanaka, *J. Phys. Chem. A* 2007**, 111***,* 2951.

Supplementary information

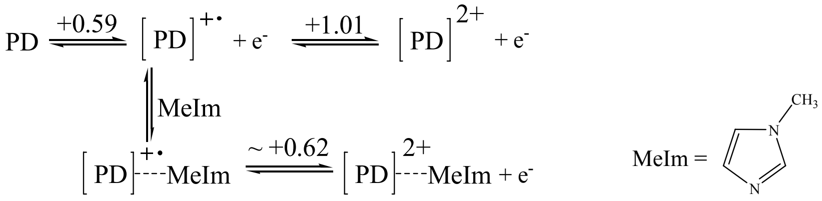
Scheme S1. Synthesis of ZnTMP-PD.



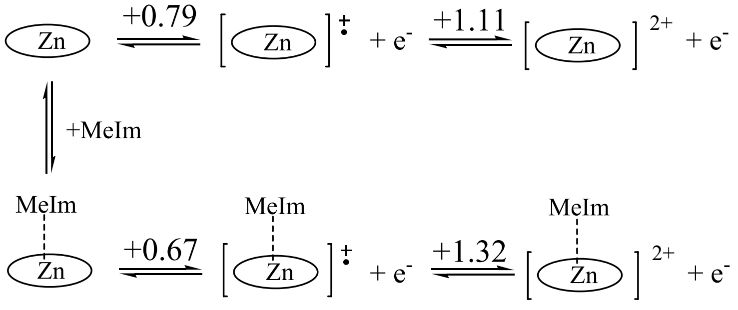
Scheme S2.

$$\text{ZnTMP-PD} \xrightleftharpoons{+0.58\text{ V}} \left[\text{ZnTMP-PD}\right]^{+} + e^{-} \xrightleftharpoons{+0.81\text{ V}} \left[\text{ZnTMP-PD}\right]^{2+} + e^{-} \xrightleftharpoons{+1.13\text{ V}} \left[\text{ZnTMP-PD}\right]^{4+} + 2e^{-}$$

Scheme S3.[S7]



Scheme S4.



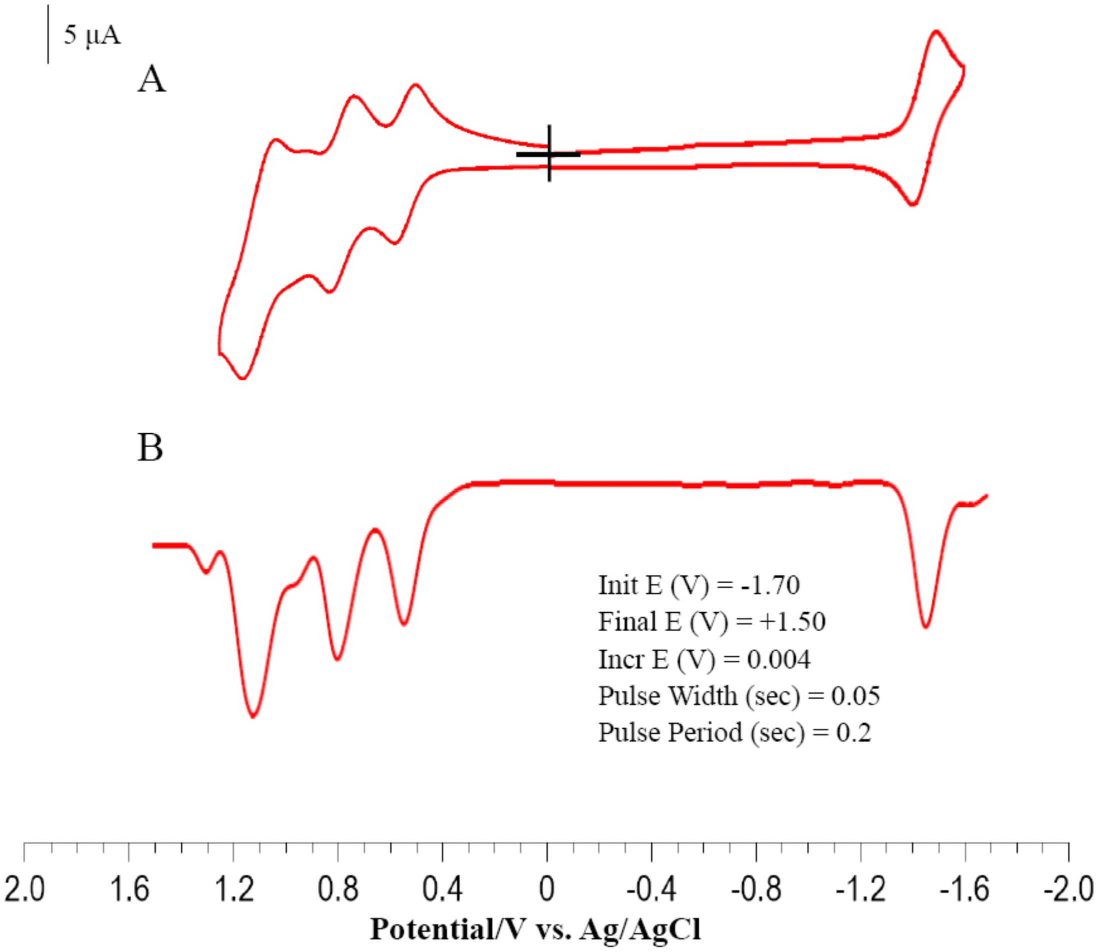


Figure S1. (A) Cyclic voltammetry and (B) Differential pulse voltammetry of 1.0 x 10^{-3} M ZnTMP-PD in CH_2Cl_2 containing 0.1 M TBAP. Working electrode：glassy carbon. Scan rate：0.1 V/s.

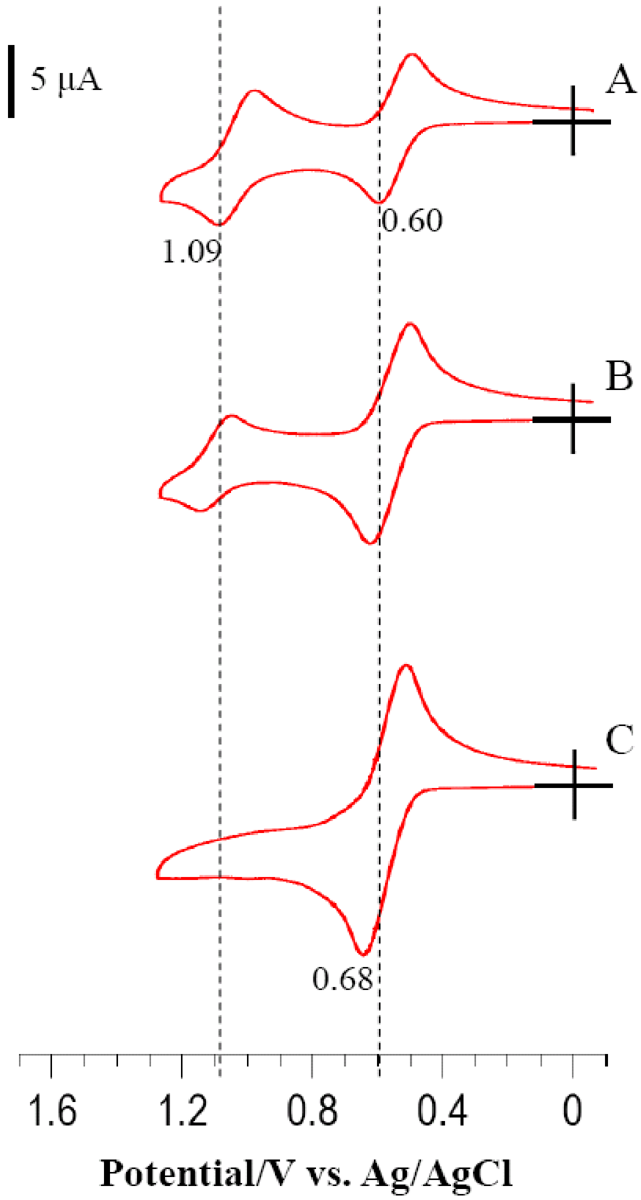


Figure S2. Cyclic voltammetry of 1.0 x 10^{-3} M PD in the presence of *N*-methylimidazole in CH_2Cl_2 containing 0.1 M TBAP. [MeIm] = (A)0.00 (B)0.50 (C)1.00 equiv. of PD. Working electrode：glassy carbon. Scan rate：0.1 V/s.

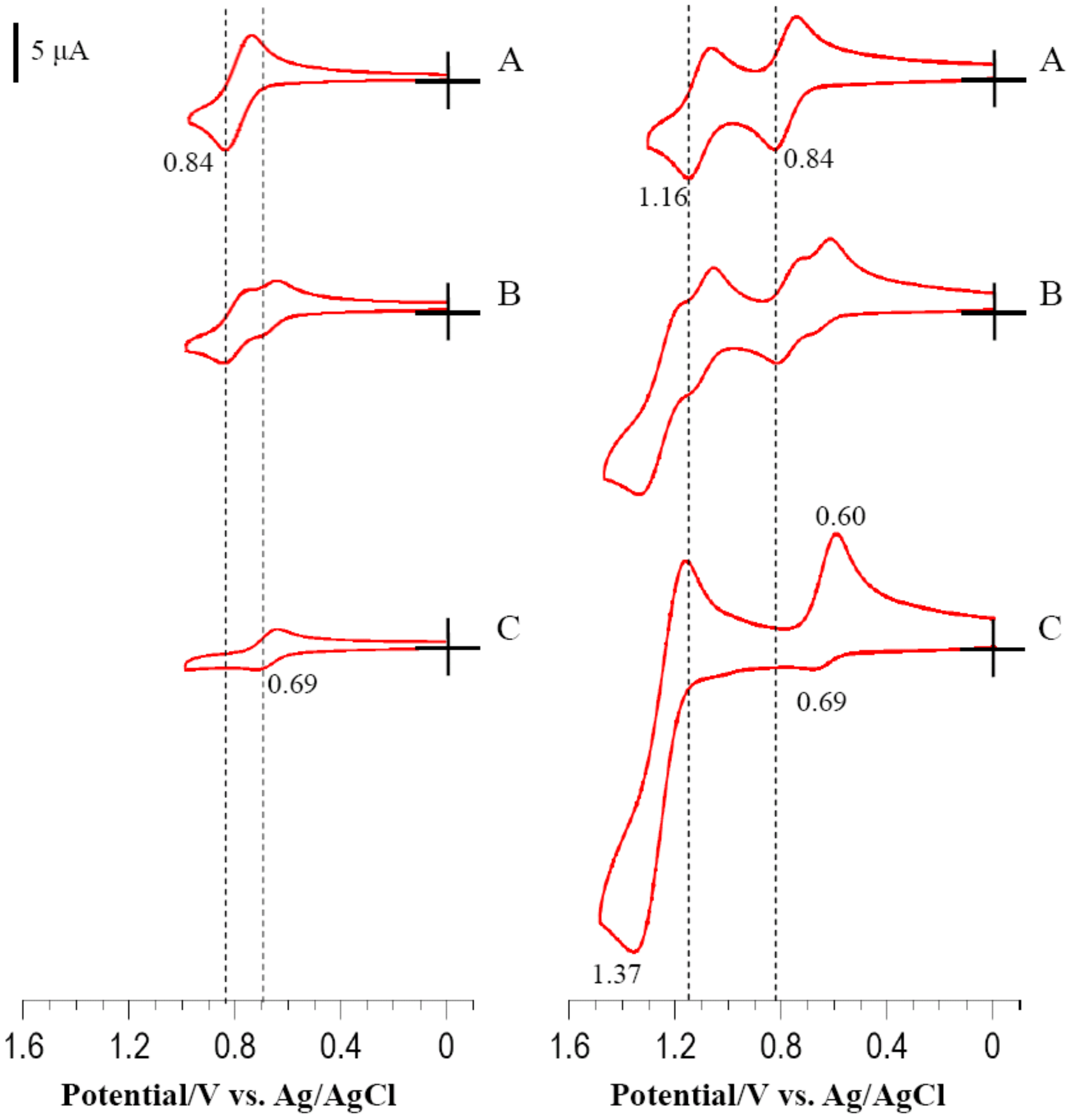


Figure S3. Cyclic voltammetry of 1.0 x 10^{-3} M ZnTMP in the presence of *N*-methylimidazole in CH_2Cl_2 containing 0.1 M TBAP. [MeIm] = (A)0.00 (B)0.50 (C)1.00 equiv. of ZnTMP. Working electrode：glassy carbon. Scan rate：0.1 V/s.

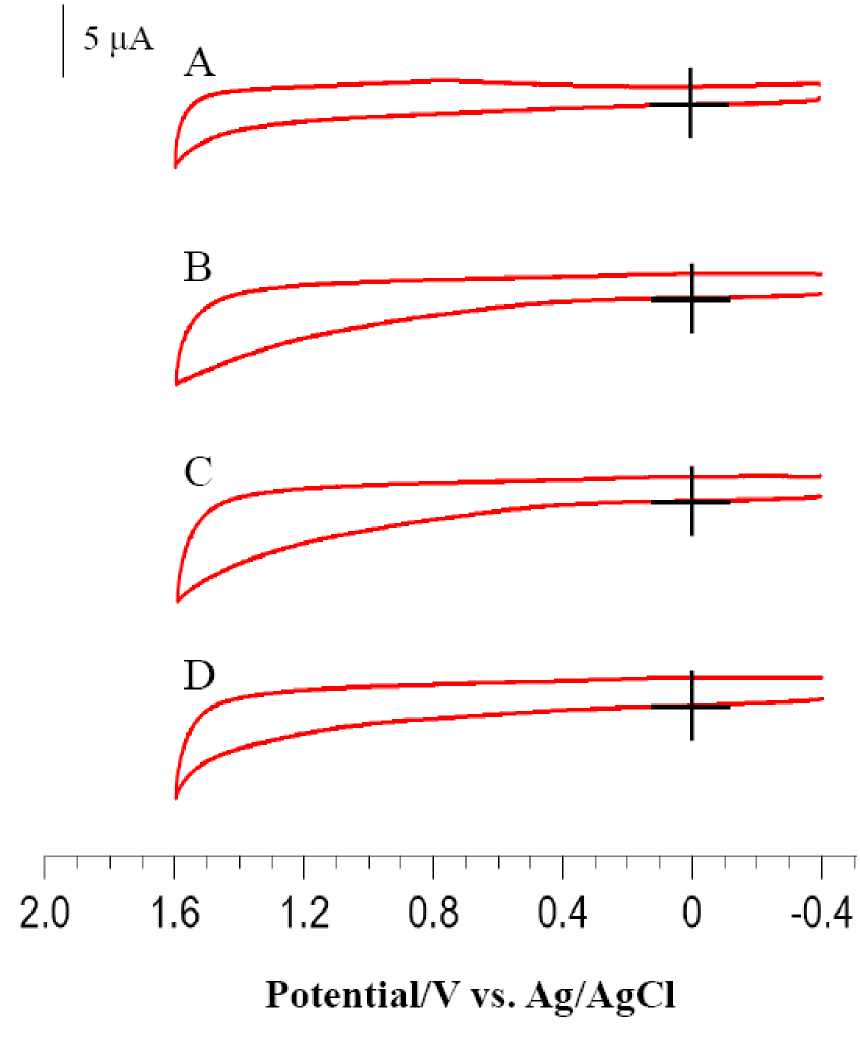


Figure S4. Cyclic voltammetry of N-methylimidazole (A)0.00 (B)0.50 x 10^{-3} (C)1.00 x 10^{-3} (D)1.5 x 10^{-3} M in CH_2Cl_2 containing 0.1 M TBAP. Working electrode：glassy carbon. Scan rate：0.1 V/s.

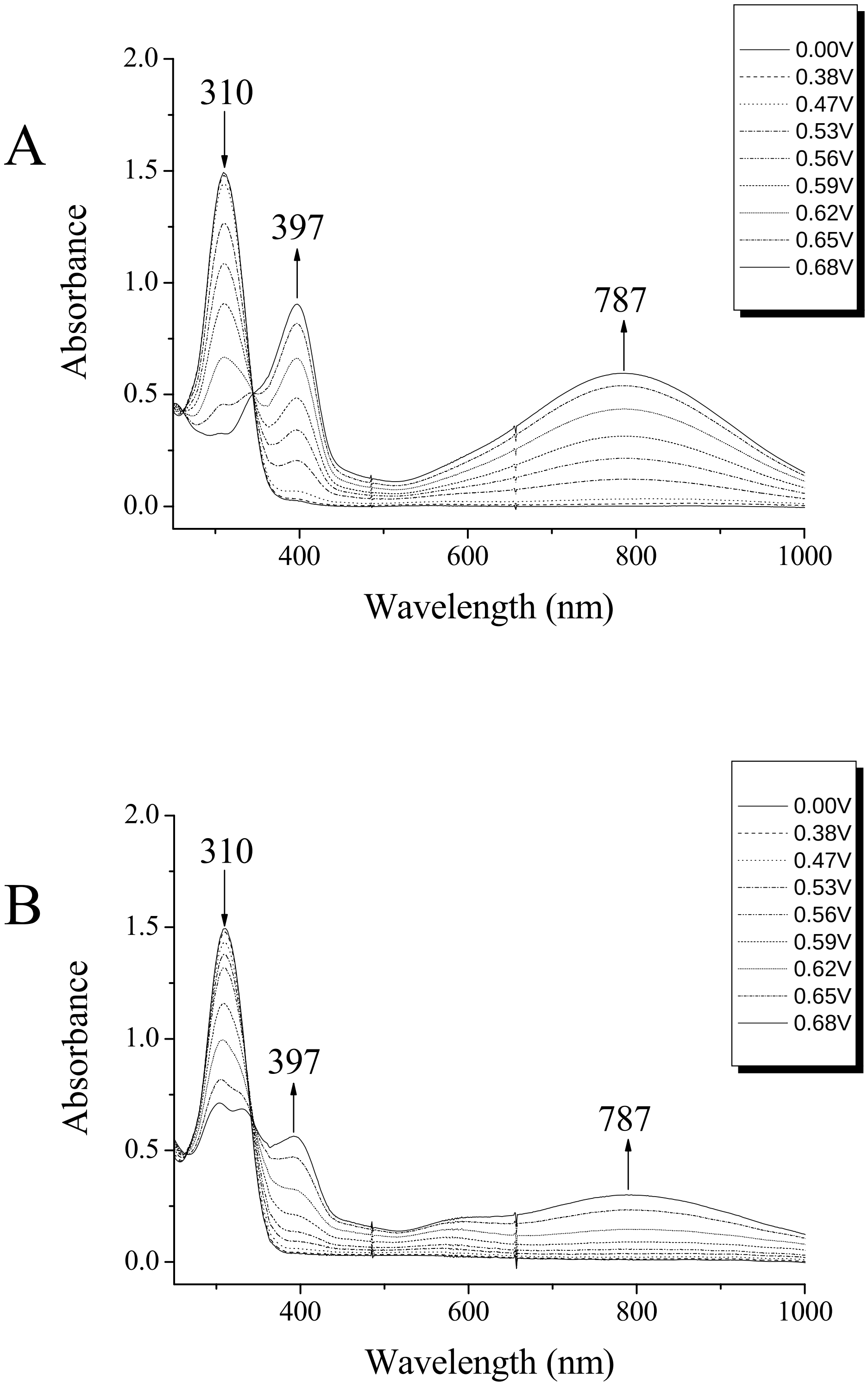


Figure S5. Spectral changes of 5.0×10^{-4} M PD in the absence (A) and presence (B) of 0.75 equiv. *N*-methylimidazole in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials.

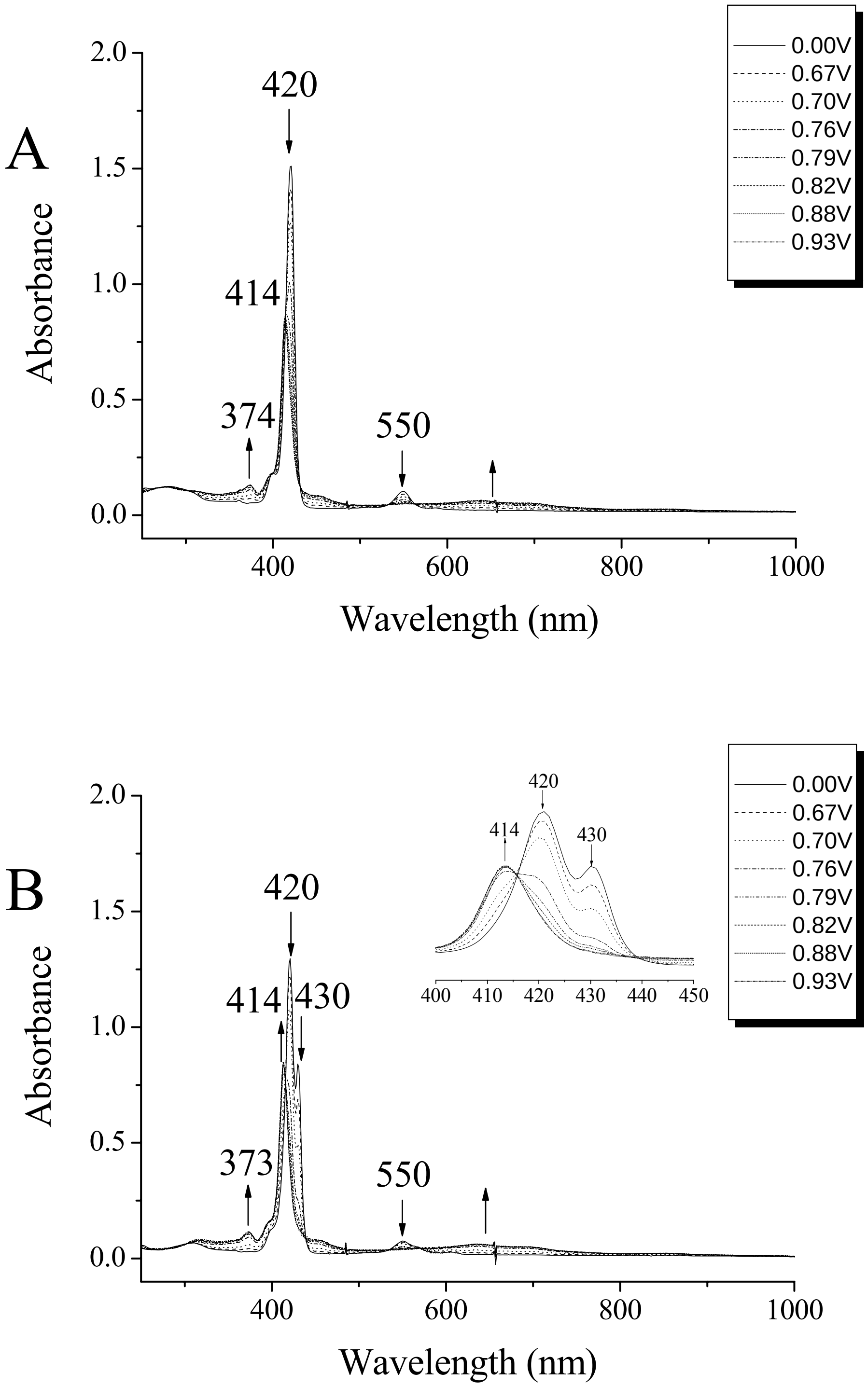


Figure S6. Spectral changes of 2.5×10^{-5} M ZnTMP in the absence (A) and presence (B) of 0.75 equiv. *N*-methylimidazole in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials.

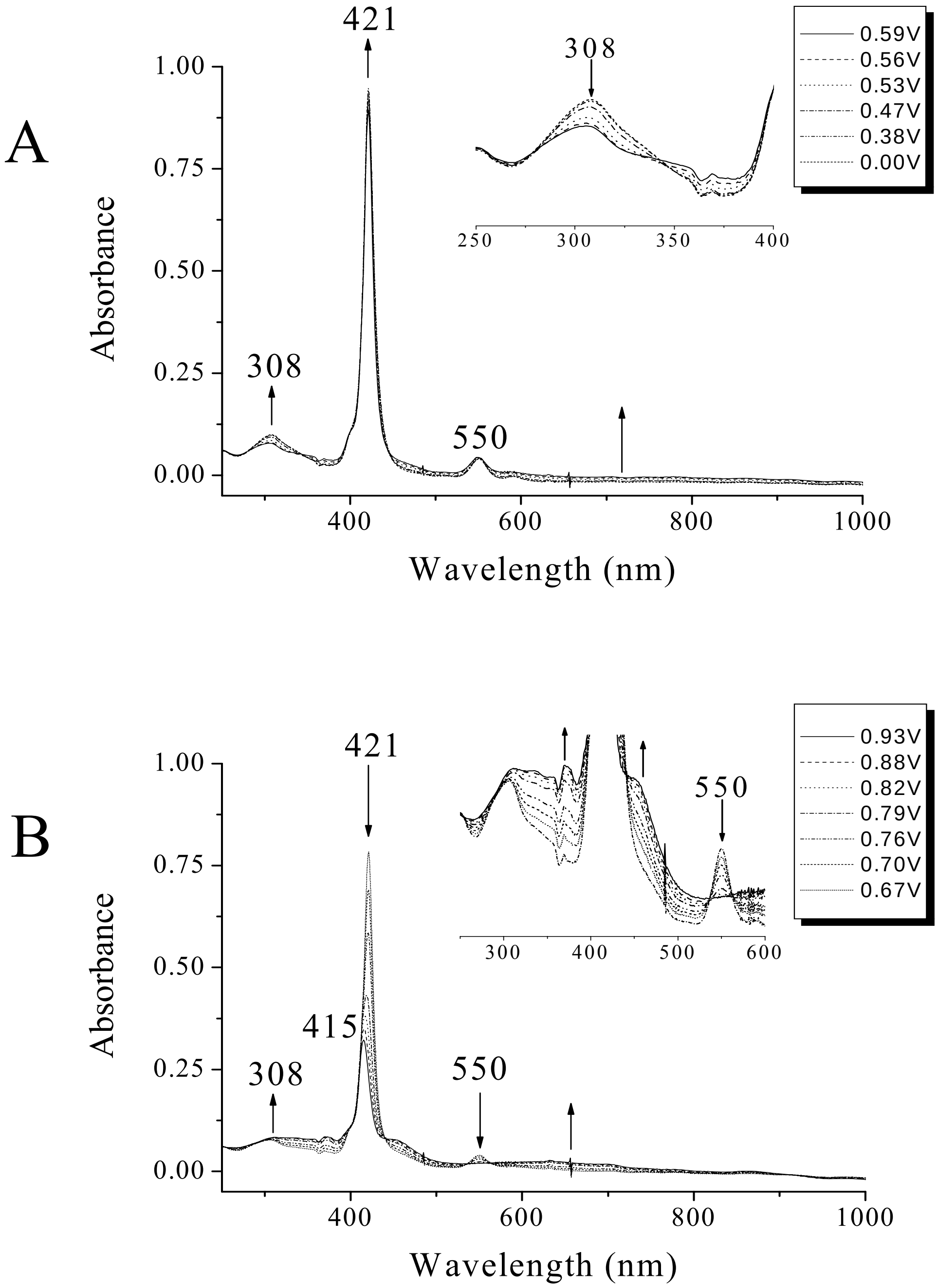


Figure S7. Spectral changes of 2.0×10^{-5} M ZnTMP-PD in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials.

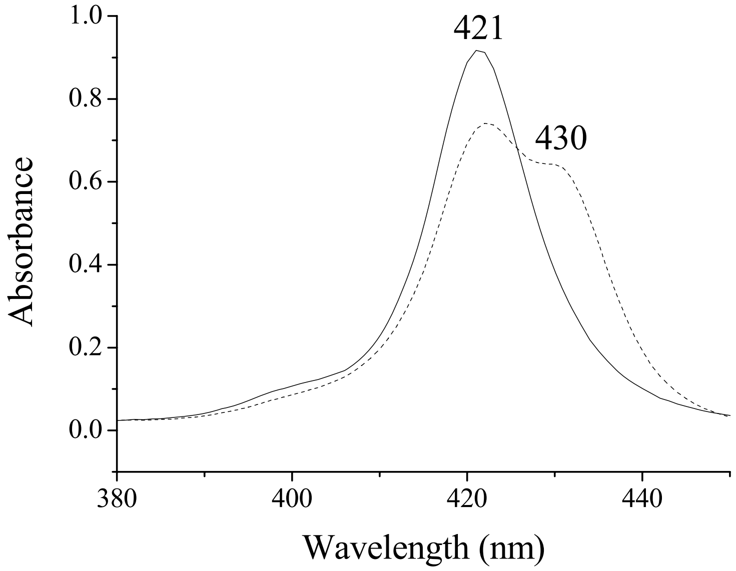


Figure S8. Spectral changes of 2.0×10^{-5} M ZnTMP-PD in the absence (solid line) and presence (dash line) of 0.75 equiv. *N*-methylimidazole in CH_2Cl_2.

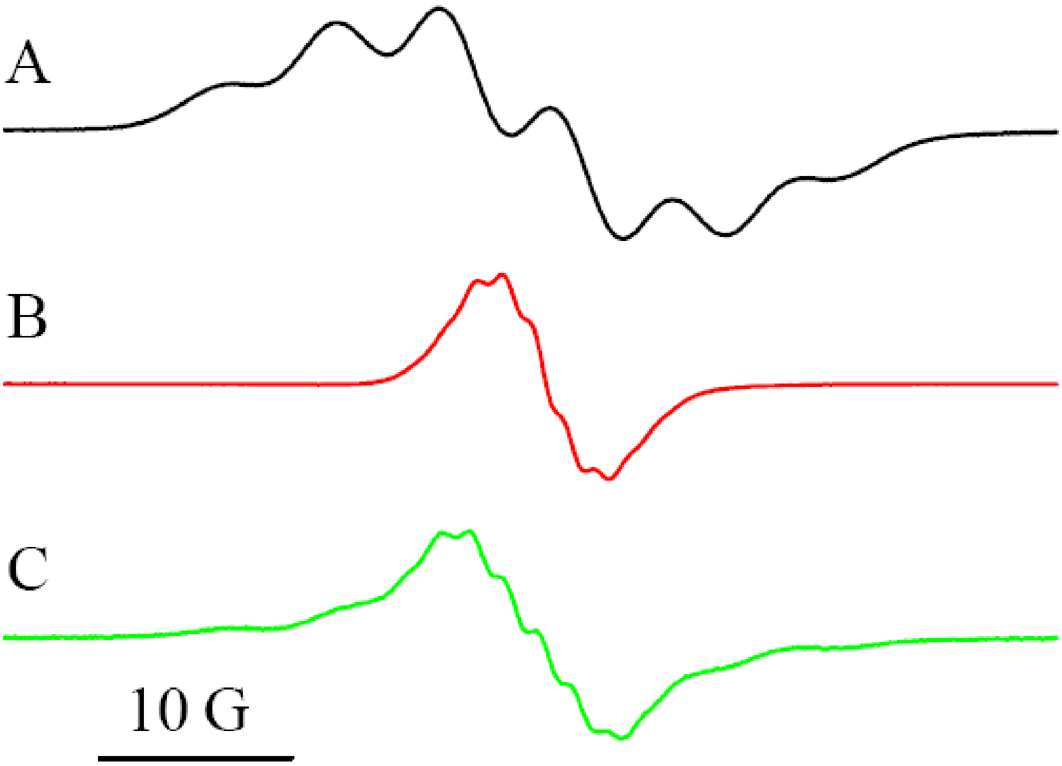


Figure S9. EPR spectra of (A)PD$^{+\cdot}$, (B)ZnTMP$^{+\cdot}$ and (C)ZnTMP-PD$^{+\cdot}$ at 298K.