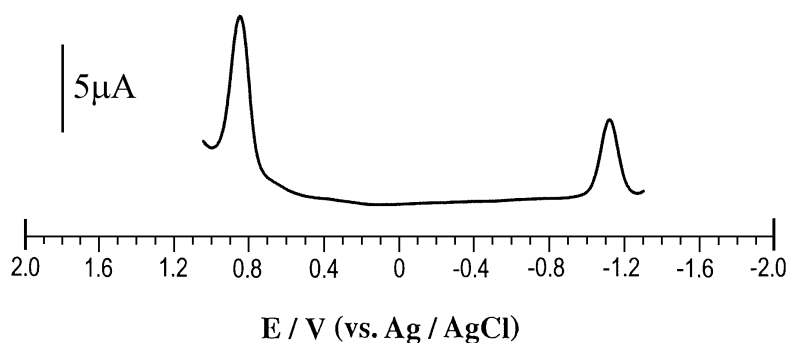


Table. Absorption spectral bandwidth ( $w^a$ ,  $\text{cm}^{-1}$ ) and oscillator strengths ( $f$ ) of zinc porphyrins in  $\text{CH}_2\text{Cl}_2$ .

compound	B band		Q <sub>1</sub> band		Q <sub>2</sub> band	
	w	f	w	f	w	f
ZnTPP	667	1.30	590	0.0616	524	0.0066
ZnTAPP <sup>c</sup>	933	1.70	680	0.0647	625	0.0508
ZnTDPAPP	1905	1.51	695	0.0699	714	0.0476
ZnTDTAPP	3009	1.69	733	0.0714	790	0.0623

- a. Taken as the spectral width of the B band and Q band region at the half of the height.  
b.  $f$  is the oscillator strength which is calculated using the equation:  
 $f = 4.319 \times 10^{-9} A/n$ , where  $A$  is the integrated absorption band (plotted as  $\epsilon$  vs.  $\text{cm}^{-1}$ ) and  $n$  is the solvent refractive index (1.42 for  $\text{CH}_2\text{Cl}_2$ )  
c. In acetone ( $n = 1.36$ ).



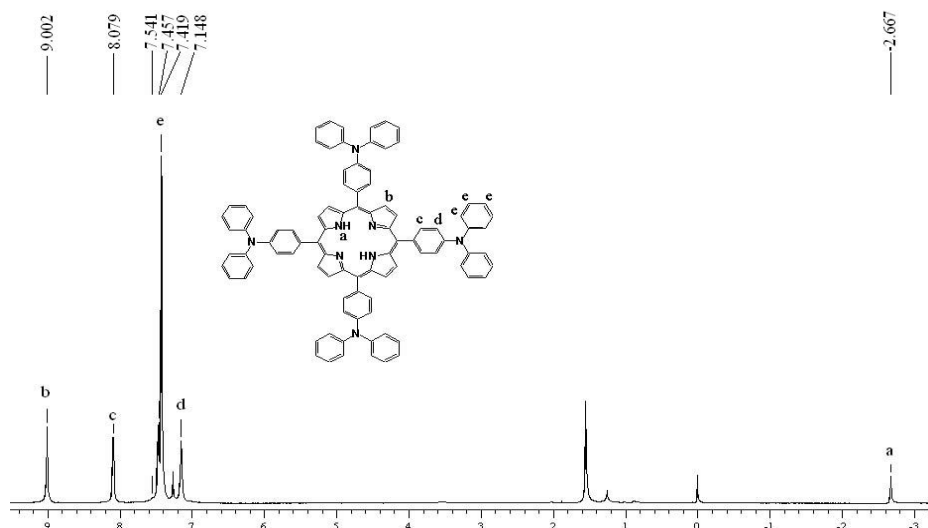
**Fig.** Differential pulse voltammograms of  $1 \times 10^{-3}$  M  $\text{H}_2\text{TDPAPP}$  in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M TBAP.  
Init. E : 1.0 V, Final E : -1.37 V, Incr. E : 0.004 V, Amplitude : 0.05 V, Pulse Width : 0.05 s,  
Sampling Width : 0.0167 s, Pulse Period : 0.1 s.

#### Synthesis of $\text{H}_2\text{TDPAPP}$

A 1 L three-neck round-bottomed flask fitted with a septum, reflux condenser, and nitrogen inlet port was charged with 500 mL of  $\text{CHCl}_3$  (distilled from  $\text{K}_2\text{CO}_3$ ), 4-diphenylaminobenzaldehyde (1.367 g, 5 mmol), and pyrrole (0.35 mL, 5 mmol). After the solution was purged with  $\text{N}_2$  for 5 min,  $\text{BF}_3 \cdot \text{OEt}_2$  (0.43 mL, 1.06 mmol) was added via syringe. The

room temperature reaction was monitored with UV/Vis spectrometry and oxidizing with excess DDQ, followed by absorption spectrophotometry. At the end of 1 h, triethylamine (0.23 mL, 1.65 mmol) was added, and the solution was rotary evaporated to dryness. The crude dry product was scraped from the flask, placed on a filter, and washed with methanol (200 mL) until the filtrate was clear. The poly-pyrromethenes and quinone components are highly soluble in methanol and are removed with ease. The final product was purple solid and recrystallized by CH<sub>2</sub>Cl<sub>2</sub> and hexane. (0.32g, yield 25%).

UV-Vis (in CH<sub>2</sub>Cl<sub>2</sub>, λ<sub>max</sub>): 438 (soret), 524, 569 and 656 nm. <sup>1</sup>H NMR (in CDCl<sub>3</sub>, δ, ppm) □ 9.00 (s, 8H, pyrrole-H, H<sub>b</sub>), 8.08 (d, J = 7.8 Hz, 8H, H<sub>c</sub>), 7.42~7.46 (m, 40H, H<sub>e</sub>), 7.15 (d, J = 7.6 Hz, 8H, H<sub>d</sub>), -2.68 (s, 2H, NH, H<sub>a</sub>). Calcd. for C<sub>92</sub>H<sub>66</sub>N<sub>8</sub> (1283.54): C, 86.09; H, 5.18; N, 8.73. Found: C, 85.65; H, 5.16; N, 8.36.

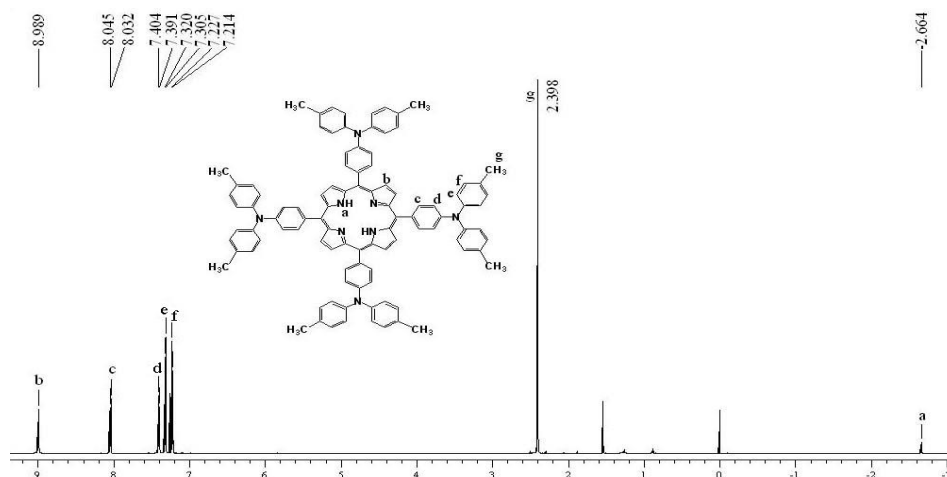


#### Synthesis of H<sub>2</sub>TDTAPP

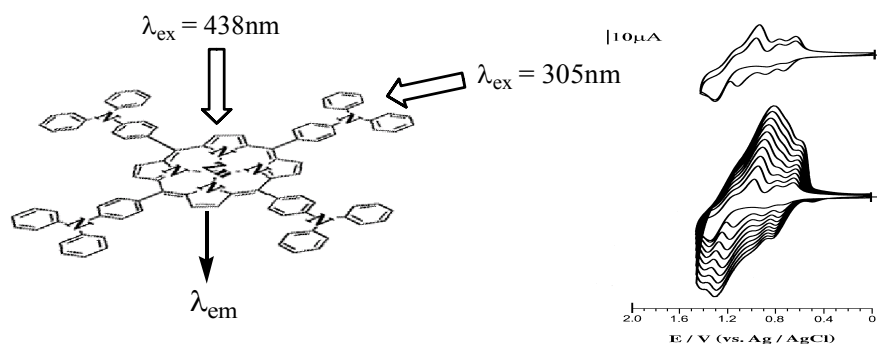
To a 250 mL round bottomed flask containing 129 mL of CHCl<sub>3</sub> equipped with a mechanical stirrer, nitrogen gas was purged for 5 min. To this 4-(di-p-tolylamino)benzaldehyde (0.39 g, 1.29 mmol) and pyrrole (0.09 mL, 1.29 mmol) were

added. After 5 min the reaction mixture was treated with  $\text{BF}_3 \cdot \text{OEt}_2$  (0.11 mL, 0.87 mmol). The nitrogen atmosphere was removed and stirring continued for 1 h. The resulting solution was treated with triethylamine (0.59 mL, 4.19 mmol). The solvent was removed by rotary evaporation. The product was subjected to further purification by methanol washing and finally by column chromatography (basic alumina,  $\text{CHCl}_3$ ). Yield (80 mg, 10 %).

UV-Vis (in  $\text{CHCl}_3$ ,  $\lambda_{\text{max}}$ ): 408 (sh), 444 (Soret), 525, 575 and 664 nm.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ , ppm) 2.40 (s, 24 H,  $\text{CH}_3$ ,  $\text{H}_g$ ), 8.04 (d,  $J = 7.8$  Hz, 8H,  $\text{H}_c$ ), 7.40 (d,  $J = 8.1$  Hz, 8H,  $\text{H}_d$ ), 7.31 (d,  $J = 9.0$  Hz, 16 H,  $\text{H}_f$ ), 7.22 (d,  $J = 8.0$  Hz, 16 H,  $\text{H}_e$ ), 8.99 (s, 8H, pyrrole-H,  $\text{H}_b$ ), -2.66 (s, 2H, NH,  $\text{H}_a$ ). Calcd. for  $\text{C}_{104}\text{H}_{98}\text{N}_8$ : C, 85.56; H, 6.77; N, 7.68. Found: C, 85.69, H, 6.30; N, 7.86.



a graphical content



In this study, electrochemical and spectral properties of porphine free bases linked with four *meso*-triphenylamine moieties and the corresponding zinc complexes are first reported. The TPA substituents slightly interact with the porphine cores revealed by the absorption spectra, fluorescence spectra and cyclic voltammograms. Intramolecular energy transfer occurs when the zinc porphyrins were excited at the wavelength where the TPA moieties absorbed. Electrooxidative polymerization of porphine-TPA conjugative systems is also found. The abundant spectral and electrochemical properties make the new hybrid system a new candidate for photosynthesis and catalysis.