Synthesis, Spectral and Electrochemical Studies of Electronically Tunable β-Substituted Porphyrins with Mixed Substituent Pattern

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Experimental Section

All commercially available chemicals were purchased from appropriate sources and used as received unless otherwise mentioned. Freshly recrystallised N-bromosuccinimide was used for bromination reactions. 2-nitro-12,13-dibromo-*meso*-tetraphenylporphyrin, 2-nitro-7,8,12,13,17,18-hexabromo-*meso*-tetraphenylporphyrinato copper(II) and its free base were synthesized by modified literature methods.[1] Mixed substituted porphyrins, $ZnTPP(NO_2)(PE)_2$, $ZnTPP(NO_2)Br_2$, and $H_2TPP(NO_2)(Th)_2$ were crystallized by the direct diffusion of CH_3OH to a saturated porphyrin solution in $CHCl_3$ over a period of 10 - 15 days. X-ray quality single crystals of $NiTPP(NO_2)Ph_2$ was obtained by direct diffusion of hexane to a saturated porphyrin solution in $CHCl_3$ containing a few drops of pyridine over a period of seven days. Crystal of $NiTPP(NO_2)Br_6$ were obtained by vapor diffusion of hexane into the saturated solution of porphyrin in 1,2-dichloroethane containing a few drops of pyridine. The single crystals obtained were mounted on mounting loops. All diffraction data were collected by using a Bruker APEXII diffractometer at 25 °C equipped with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) by the ω-2θ scan. The structures were solved by direct methods by using SIR97 and SHELX-97.[2] Crystallographic data for these compounds are summarized in Table S1 in the supporting information. CCDC- 1018319 ($NiTPP(NO_2)Ph_2$), -1018393 ($ZnTPP(NO_2)(PE)_2$), - 1018509 ($H_2TPP(NO_2)(Th)_2$), - 1019075 ($ZnTPP(NO_2)Br_2$), and -1019824 ($NiTPP(NO_2)Br_6$ contain the supplementary crystallographic data. The ground state geometries of mixed substituted free base porphyrins ($H_2TPP(NO_2)X_6$ and $H_2TPP(NO_2)X_2$) were optimized in the gas phase by DFT calculations with B3LYP functional and LANL2DZ basis set using Gaussian 09.

UV-Vis absorption spectra were measured in distilled dichloromethane using Shimadzu UV-1800 spectrometer at 298 K. The fluorescence spectra were carried out using Hitachi F-4600 spectroflurometer in CH_2Cl_2. All ^1H NMR measurements were performed using Bruker AVANCE 500 spectrometer in $CDCl_3$. MALDI-TOF-MS spectra were measured using a Bruker UltrafleXtreme-TN MALDI-TOF/TOF spectrometer using dithranol as a matrix and ESI mass spectra were recorded using Bruker Daltanics-microTOF. The elemental analysis was carried out on Elementarvario EL III instrument. Cyclic voltammetric measurements were carried out using BAS Epsilon and CH 620E electrochemical workstation. A three electrode system was used and consisted of a Pt button working electrode (0.2 mm diameter), Ag/AgCl reference electrode and a Pt-wire counter electrode. The concentrations of all porphyrins employed were ~1 mM. All measurements were performed in triple distilled CH_2Cl_2 solution which was purged with Ar gas, using 0.1 M $TBAPF_6$ as the supporting electrolyte.

The stoichiometry and binding constants for protonation were analyzed by Hill equation.[3]

$\log[(A_n-A_0)/(A_f-A_n)] = \log \beta_2 + n\log[TFA]$

The Hill plot was constructed by plotting $\log[(A_n-A_0)/(A_f-A_n)]$ versus $\log[TFA]$ where A_0 and A_n are the absorbance values of porphyrin employed and protonated species, respectively at a given concentration of the TFA added. A_f denotes the absorbance of the diprotonated species at a particular wavelength. The slope of the line (n) was found to be two for one-to-two stoichiometry between the porphyrin and the added TFA. The value of $\log\beta_2$ is evaluated from the intercept of the line at $\log[(A_n-A_0)/(A_f-A_n)] = 0.0$. In the present study, the $\log\beta_2$ values were evaluated by using a minimum of two wavelengths and an average value of n and $\log\beta_2$ is reported. The similar methodology was employed for deprotonation studies also.

I. Synthesis of MTPP(NO_2)X_2 (X = Br, Ph, Th, PE and CN) derivatives:

(a) Synthesis of 2-nitro-12,13-dibromo-*meso*-tetraphenylporphyrin[1] and its metal complexes

2-nitro-*meso*-tetraphenylporphyrin (0.220 g, 0.447 mmol, 1 equiv.) was taken in 45 mL of distilled $CHCl_3$. To this, freshly recrystallized NBS (0.148 g, 1.119 mmol) was added and refluxed for 72 hrs. Solvent was rotary evaporated to dryness under vacuum. The crude porphyrin was purified on silica column using $CHCl_3$ as eluent. Yield was found to be 81% (0.220 g).

H_2TPP(NO_2)Br_2: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.97 (s, 1H, β-pyrrole-H), 8.84 (t, 3H, J = 5 Hz, β-pyrrole-H), 8.78 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.28 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 8.22 (d, 2H, J = 7 Hz *meso-o*-phenyl-H), 8.16 (t, 4H, J = 8.5 Hz, *meso-o*-phenyl-H),7.85-7.70 (m, 12H, *meso-m- and p*-phenyl-H), -2.63 (bs, 1H, imino-H), -2.68 (bs, 1H, imino-H). ESI-MS (m/z): found 818.10 $[M+H]^+$, calcd. 818.22. Anal. Calcd for $C_{44}H_{27}N_5O_2Br_2$•0.5 $CHCl_3$: C, 60.93; H, 3.16; N, 7.98%. Found: C, 60.69; H, 3.34; N, 7.66%.

H_2TPP(NO_2)Br_2 (0.0183mmol) was dissolved in 10 mL of $CHCl_3$. To this, 10 equiv. of $M(OAc)_2$•nH_2O (M = Cu(II), Zn(II), Co(II), 10 equiv.) in 2 mL of methanol was added and refluxed for 40 minutes and then cooled to room temperature, washed with water, dried over anhydrous sodium sulphate. The crude product was purified by column chromatography on silica column using $CHCl_3$ as eluent. Further, Ni(II) complexes were prepared by refluxing H_2TPP(NO_2)Br_2 and $Ni(OAc)_2$•$2H_2O$ (10 equiv.) in DMF[22] for 2 hours followed by the precipitation with water. The crude product was purified on silica column using $CHCl_3$ as eluent. Yield was found to be 80 - 90%.

NiTPP(NO_2)Br_2: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.90 (s, 1H, β-pyrrole-H), 8.64 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.58 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.51 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.45 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.02-7.92 (m, 4H, *meso-o*-phenyl-H), 7.85 (d, 4H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.75-7.59 (m, 12H, *meso-m- and p*-phenyl-H). MALDI-TOF-MS (m/z): found 874.54 $[M^+]$, calcd. 874.22. Anal. Calcd for $C_{44}H_{25}N_5O_2Br_2Ni$•$2H_2O$: C, 58.38; H, 2.67; N, 7.73%. Found: C, 58.11; H, 2.80; N, 7.47%. **CuTPP(NO_2)Br_2**: MALDI-TOF-MS (m/z): found 879.48 $[M^+]$, calcd., 879.07. **ZnTPP(NO_2)Br_2:** ^{1}H NMR in $CDCl_3$: δ (ppm) 9.14 (s, 1H, β-pyrrole-H), 8.85 (dd, 2H, *Ja* = 8 Hz, *Jb* = 4.5 Hz β-pyrrole-H), 8.81-8.75 (m, 2H, β-pyrrole-H), 8.16 (t, 4H, J = 6 Hz, *meso-o*-phenyl-H), 8.03 (d, 4H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.84-7.64 (m, 12H, *meso-m- and p*-phenyl-H). MALDI-TOF-MS (m/z): found 881.25 $[M^+]$, calcd. 880.91. **CoTPP(NO_2)Br_2:** ESI-MS (m/z): found 873.99 $[M^+]$, calcd. 874.46.

(b) Synthesis of 2-nitro-12,13-diphenyl-*meso*-tetraphenylporphyrin and its metal complexes

Two-way stoppered RB flask was charged with H_2TPP(NO_2)Br_2 (0.16 g, 0.196 mmol), phenyl boronic acid (0.284 g, 2.33 mmol) and K_2CO_3 (0.648 g, 4.68 mmol). To this, 50 mL of distilled toluene was added and purged with Ar gas for 10 minutes. Then $Pd(PPh_3)_4$(0.045 g, 0.039 mmol) was added under Ar and heated to 100℃ for 18 hrs. After completion of the reaction, the solvent was removed by rotary evaporation. The residue was redissolved in $CHCl_3$ (50 mL) and washed with saturated $NaHCO_3$ (50 ml) followed by 30% NaCl solution (50 ml). Finally, the organic

layer was dried over anhydrous Na_2SO_4. The crude product was purified on silica column using variant polarity from $CHCl_3$/hexane mixture (3:1, v/v) to 100% $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3/CH_3OH$ mixture (1:3, v/v). The yield was found to be 0.130 g (71%).

H_2TPP(NO_2)Ph_2: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.98 (s, 1H, β-pyrrole-H), 8.81 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.78 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.58 (t, 2H, J = 5 Hz, β-pyrrole-H), 8.30 (dd, 2H, J = 7.5 Hz, J = 1.5 Hz, *meso-o*-phenyl-H), 8.23 (dd, 2H, J = 7.5 Hz, J = 1.5 Hz, *meso-o*-phenyl-H), 7.85 (d, 2H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.80 (t, 5H, J = 8.0 Hz, *meso-o and m*-phenyl-H), 7.74 (d, 3H, J = 7.5 Hz, *meso-o and m*-phenyl-H), 7.33-7.21 (m, 6H, *meso-m- and p*-phenyl-H), 6.90-6.80 (m, 10H, β-pyrrolePh-H), -2.31 (bs, 1H, imino-H). ESI-MS (m/z): found 812.34 [M^+], calcd. 812.39. Anal. Calcd for $C_{56}H_{37}N_5O_2$: C, 82.84; H, 4.59; N, 8.62%. Found: C, 82.98; H, 4.27; N, 8.34%.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of MTPP(NO_2)Br_2. The yield was found to be 85 - 95%. **NiTPP(NO_2)Ph_2:** ^{1}H NMR in $CDCl_3$: δ (ppm) 8.92 (s, 1H, β-pyrrole-H), 8.54 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.42 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.29 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.23 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.00-7.94 (m, 4H, *meso-o*-phenyl-H), 7.73-7.58 (m, 6H, *meso-m*-phenyl-H), 7.48 (d, 2H, J = 7.0 Hz, *meso-o*-phenyl-H), 7.42 (d, 2H, J = 7.0 Hz, *meso-o*-phenyl-H), 7.19 (AB quartet, 2H, J = 8.0 Hz, *meso-m*-phenyl-H), 7.09 (t, 4H, J = 7.5 Hz, *meso-p*-phenyl-H), 6.95-6.76 (m, 10H, β-pyrrolePh-H). MALDI-TOF-MS (m/z): found 868.98 [M^+], calcd. 868.62. Anal. Calcd for $C_{56}H_{35}N_5O_2Ni$•0.5CH_3OH: C, 76.71; H, 4.22; N, 4.52%. Found: C, 76.98; H, 4.36; N, 4.74%. **ZnTPP(NO_2)Ph_2:** ^{1}H NMR in $CDCl_3$: δ (ppm) 9.12 (s, 1H, β-pyrrole-H), 8.80 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.755 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.53-8.51 (m, 2H, β-pyrrole-H), 8.21 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 8.18 (d, 2H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.80-7.70 (m, 8H, *meso-o*-phenyl-H), 7.67 (at, 2H, J = 7.5 Hz, *meso-m*-phenyl-H), 7.24-7.22 (m, 2H, *meso-m*-phenyl-H), 7.15 (dt, 4H, J = 7.5Hz, J = 2.5Hz, *meso-p*-phenyl-H), 6.93 (d, 4H, J = 7.5 H, β-pyrrolePh-*o*-H), 6.90-6.80 (m, 6H, β-pyrrolePh-*m- and p*-H). MALDI-TOF-MS (m/z): found 875.51 [M^+], calcd. 875.32. Anal. Calcd for $C_{56}H_{35}N_5O_2Zn$: C, 76.84; H, 4.03; N, 8.00%. Found: C, 76.69; H, 4.04; N, 7.78%. **CuTPP(NO_2)Ph_2:** Anal. Calcd for $C_{56}H_{35}N_5O_2Cu$: C, 75.61; H, 4.34; N, 7.73%. Found: C, 75.52; H, 4.26; N, 7.44%. MALDI-TOF-MS (m/z): found 873.91 [M^+], calcd. 873.47. **CoTPP(NO_2)Ph_2:** ESI-MS (m/z): found 868.23 [M^+], calcd., 868.86.

(c) Synthesis of 2-nitro-12,13-diphenylethynyl-*meso*-tetraphenylporphyrin and its metal complexes

H_2TPP(NO_2)Br_2 (0.3 g, 0.366 mmol), $Pd(PPh_3)_4$ (0.084 g, 0.073 mmol) were dissolved in distilled 1,4-dioxane (90 mL) and purged with argon gas for 15 minutes. To this, tributyl(phenylethynyl)stannane (0.406 mL, 1.158 mmol) in 42 mL of degassed dioxane was added and heated to 80℃ for 3 hrs under argon atmosphere. After completion of the reaction, the solvent was removed by vacuum distillation. The crude porphyrin was redissolved in $CHCl_3$ (20 mL) and purified on silica column using variant polarity from $CHCl_3$/hexane mixture (3:2, v/v) to 100% $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3/CH_3OH$ mixture (1:3, v/v) containing one drop of Et_3N. The yield was found to be 0.210 g (73%).

$H_2TPP(NO_2)(PE)_2$: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.99 (s, 1H, β-pyrrole-H), 8.90 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.86 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.77 (d, 1H, J = 5.5 Hz, β-pyrrole-H), 8.76 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.30-8.18 (m, 8H, *meso-o*-phenyl-H), 7.85-7.68 (m, 12H, *meso-m and p*-phenyl-H), 7.38-7.26 (m, 10H, β-pyrrole-PE-H), -2.51 (s, 1H, imino-H), -2.54 (s, 1H, imino-H). ESI-MS (m/z): found 860.27 [M^+], calcd. 859.99. Anal. Calcd for $C_{60}H_{37}N_5O_2$•$2H_2O$: C, 80.43; H, 4.61; N, 7.82%. Found: C, 80.83; H, 4.37; N, 7.83%. The metal complexes were prepared with similar procedures of the corresponding metal complexes of $MTPP(NO_2)Br_2$ and the yields were found to be 80 - 85%.

$NiTPP(NO_2)(PE)_2$: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.91 (s, 1H, β-pyrrole-H), 8.61 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.60 (d, 1H, J = 5.5 Hz, β-pyrrole-H), 8.52 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.45 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.02-7.94 (m, 8H, *meso-o*-phenyl-H), 7.75-7.58 (m, 12H, *meso-m and p*-phenyl-H), 7.33-7.26 (m, 10H, β-pyrrole-PE-H). MALDI-TOF-MS (m/z): found 917.02 [M^+], calcd. 916.66. Anal. Calcd for $C_{60}H_{35}N_5O_2Ni$: C, 78.62; H, 3.85; N, 7.64%. Found: C, 78.58; H, 3.94; N, 7.47%. **$ZnTPP(NO_2)(PE)_2$:** ^{1}H NMR in $CDCl_3$: δ (ppm) 9.14 (s, 1H, β-pyrrole-H), 8.88 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.85 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.74 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.73 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.21-8.13 (m, 8H,*meso-o*-phenyl-H), 7.82-7.64 (m, 12H, *meso-m and p*-phenyl-H), 7.40-7.34 (m, 4H, β-pyrrole-*o*-PE-H), 7.31-7.26 (m, 6H, β-pyrrole-*m and p*-PE-H). MALDI-TOF-MS (m/z): found 923.46 [M^+], calcd. 923.36. Anal. Calcd for $C_{60}H_{35}N_5O_2Zn$•H_2O: C, 76.55; H, 3.96; N, 7.44%. Found: C, 76.24; H, 3.79; N, 7.29%. **$CuTPP(NO_2)(PE)_2$:** MALDI-TOF-MS (m/z): found 921.98 [M^+], calcd. 921.52. Anal. Calcd. for $C_{60}H_{35}N_5O_2Cu$: C, 78.42; H, 3.92; N, 7.51%. Found: C, 78.20; H, 3.83; N, 7.60%. **$CoTPP(NO_2)(PE)_2$:** ESI-MS (m/z): found 916.25 [M^+], calcd., 916.90. Anal. Calcd. for $C_{60}H_{35}N_5O_2Co$•$2H_2O$: C, 75.62; H, 4.13; N, 7.35%. Found: C, 75.45; H, 3.87; N, 7.31%.

(d) Synthesis of 2-nitro-12,13-dithienyl-*meso*-tetraphenylporphyrin and its metal complexes:

$H_2TPP(NO_2)Br_2$ (0.15 g, 0.183 mmol), thiophene-2-boronic acid (0.117 g, 0.914 mmol) and K_2CO_3 (0.609 g, 4.40 mmol) were taken in a two-way stoppered RB flask. To this, 60 mL of distilled toluene was added and purged with Ar gas for 10 minutes. Then $Pd(PPh_3)_4$ (0.042 g, 0.036 mmol) was added under Ar and heated to 90°C for 10 hrs. After completion of the reaction, the solvent was removed by rotary evaporation. The crude porphyrin was redissolved in $CHCl_3$ (50 mL) and washed with saturated $NaHCO_3$ (50 mL) followed by 30% NaCl solution (50 mL). Finally, the organic layer was dried over anhydrous Na_2SO_4. The crude product was purified on silica column using variant polarity from $CHCl_3$ to 2% EtOAc/$CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3$/CH_3OH mixture (1:3, v/v). The yield was found to be 0.085 g (56%).

$H_2TPP(NO_2)Th_2$: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.96 (s, 1H, β-pyrrole-H), 8.77 (t, 2H, J = 5.5 Hz, β-pyrrole-H), 8.68-8.59 (m, 2H, β-pyrrole-H), 8.30 (d, 2H, J = 6.5 Hz, *meso-o*-phenyl-H) , 8.24 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.99 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.95 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.84-7.70 (m, 6H, *meso-m and p*-phenyl-H), 7.46- 7.35 (m, 6H, *meso-m and p*-phenyl-H), 6.98 (s, 2H, β-pyrroleTh-H), 6.64-6.57 (m , 3H, β-pyrroleTh-H), 6.56 (s, 1H, β-pyrroleTh-H), -2.24 (s, 2H, imino-H). ESI-MS (m/z): found 824.23 [M^+], calcd. 824.00. Anal.

Calcd for $C_{52}H_{33}N_5O_2S_2 \cdot 2H_2O$: C, 72.62; H, 4.34; N, 8.14; S, 7.46%. Found: C, 72.94; H, 4.22; N, 7.91; S, 7.16%.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of $MTPP(NO_2)Br_2$ and the yields were found to be almost quantitative. **$NiTPP(NO_2)Th_2$:** ^{1}H NMR in $CDCl_3$: δ (ppm) 8.90 (s, 1H, β-pyrrole-H), 8.53 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.43 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.36 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.29 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.02-7.96 (m, 4H, *meso-o*-phenyl-H), 7.74-7.55 (m, 10H, *meso-o- and m*-phenyl-H), 7.37-7.26 (m, 3H, *meso-m- and p*-phenyl-H), 7.24-7.21 (m, 3H, *meso-p*-phenyl-H), 7.06 (d, 1H, J = 4.5 Hz, β-pyrroleTh-H), 7.02 (d, 1H, J = 5 Hz, β-pyrroleTh-H), 6.60 (t, 1H, J = 4.5 Hz, β-pyrroleTh-H), 6.53 (t, 1H, J = 4 Hz, β-pyrroleTh-H), 6.47 (d, 1H, J = 2.5 Hz, β-pyrroleTh-H), 6.36 (d, 1H, J = 2.5 Hz, β-pyrroleTh-H). MALDI-TOF-MS (m/z): found 880.94 [M^+], calcd. 880.68. **$ZnTPP(NO_2)Th_2$:** ^{1}H NMR in $CDCl_3$: δ (ppm) 9.15 (s, 1H, β-pyrrole-H), 8.82 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.79 (d, 1H, J = 4.5 Hz, β-pyrrole-H), 8.60 (t, 2H, J = 5 Hz, β-pyrrole-H), 8.18 (t, 4H, J = 8.5 Hz, *meso-o*-phenyl-H), 7.86 (t, 4H, J = 8 Hz *meso-o*-phenyl-H), 7.81-7.72 (m, 4H, *meso-m*-phenyl-H), 7.68 (t, 2H, J = 7.5 Hz *meso-m*-phenyl-H), 7.42-7.35 (m, 2H, *meso-m*-phenyl-H), 7.33- 7.28 (m, 4H, *meso-p*-phenyl-H), 7.04 (d, 2H, J = 5 Hz, β-pyrroleTh-H), 6.66-6.56 (m, 4H, β-pyrroleTh-H). MALDI-TOF-MS (m/z): found 887.59 [M^+], calcd. 887.37. **$CuTPP(NO_2)Th_2$:** MALDI-TOF-MS (m/z): found 885.89 [M^+], calcd. 885.53. Anal. Calcd for $C_{52}H_{31}N_5O_2S_2Cu$: C, 70.53; H, 3.53; N, 7.91; S, 7.24%. Found: C, 70.64; H, 3.56; N, 7.97; S, 7.51%. **$CoTPP(NO_2)Th_2$:** ESI-MS (m/z): found 880.16 [M^+], calcd. 880.13. Anal. Calcd for $C_{52}H_{31}N_5O_2S_2Co \cdot 0.5CHCl_3$: C, 67.34; H, 3.38; N, 7.45; S, 6.82%. Found: C, 67.46; H, 3.42; N, 7.41; S, 6.55%.

(e) Synthesis of 2-nitro-12,13-dicyano-*meso*-tetraphenylporphyrinato Nickel(II)

$NiTPP(NO_2)Br_2$ (0.15 g, 0.172 mmol) and copper(I)cyanide (0.307 g, 3.43 mmol) was taken in 100 mL two neck RB and to it was added 10 mL of quinoline. The reaction mixture was refluxed at 200°C for 2 hours. At the end of this period the reaction mixture was cooled and filtered through G-4 crucible to remove excess copper cyanide. 30 mL of $CHCl_3$ was added and organic phase was washed with 10% HCl (3 × 50 mL), water (2 times), dried over Na_2SO_4 and then evaporated to dryness. The crude product was loaded on silica column and purified using $CHCl_3$ as eluent. $NiTPP(NO_2)CN$ was obtained as first fraction in 24%m yield followed by $NiTPP(NO_2)(CN)_2$ in 61% yield.

$NiTPP(NO_2)(CN)_2$: ^{1}H NMR in $CDCl_3$: δ (ppm) 9.22 (s, 1H, β-pyrrole-H), 8.84-8.69 (m, 3H, β-pyrrole-H), 8.62 (d, 1H, J = 5 Hz, β-pyrrole-H), 7.92-7.81 (m, 11H, *meso-o- and m*-phenyl-H), 7.76-7.67 (m, 9H, *meso-m- and p*-phenyl-H). MALDI-TOF-MS (m/z): found 766.82 [M^+], calcd. 766.44.

(f) Synthesis of 2-nitro-12,13-dicyano-*meso*-tetraphenylporphyrin and it metal complexes

$NiTPP(NO_2)(CN)_2$ (0.07 g, 0.091 mmol) was taken in 20 mL of $CHCl_3$ and to it was added 0.1 mL of conc. H_2SO_4 dropwise, stirred vigorously at 0°C for 2 hours. At the end of this period, distilled water (40 mL) was added dropwise to the reaction mixture with constant stirring. The organic layer was separated and washed with water (2 × 30 mL) followed by neutralization using 25% aqueous ammonia solution (20 mL). The organic layer was dried over anhydrous Na_2SO_4

and concentrated to small volume. This was purified by silica gel chromatograpy using $CHCl_3$ as eluent and the yield of the product was found to be 0.05 g (77%).

$H_2TPP(NO_2)(CN)_2$: ^{1}H NMR in $CDCl_3$: δ (ppm) 9.33 (s, 1H, β-pyrrole-H), 9.02-8.94 (m, 3H, β-pyrrole-H), 8.91 (d, 1H, J = 5 Hz, β-pyrrole-H), 8.20-8.10 (m, 8H, *meso-o*-phenyl-H), 7.99-7.91 (m, 3H, *meso-m- and p*-phenyl-H), 7.88-7.77 (m, 9H, *meso-m- and p*-phenyl-H), -2.52(s, 2H, imino-H). ESI-MS (m/z): found 711.00 $[M+H]^+$, calcd. 710.77. Anal. Calcd for $C_{46}H_{27}N_7O_2$: C, 77.84; H, 3.83; N, 13.81%. Found: C, 77.66; H, 4.13; N, 13.52%.

$MTPP(NO_2)(CN)_2$ (M = Co(II), Cu(II) and Zn(II)) were prepared with similar procedures of the corresponding metal complexes of $MTPP(NO_2)Br_2$ and the yields were found to be 80 - 90%. **$ZnTPP(NO_2)(CN)_2$**: ^{1}H NMR in $CDCl_3$: δ (ppm) 9.35 (s, 1H, β-pyrrole-H), 8.89-8.79 (m, 3H, β-pyrrole-H), 8.77 (br s, 1H, β-pyrrole-H), 8.15-7.98 (m, 8H *meso-o*-phenyl-H), 7.92-7.69 (m, 12H, *meso-m- and p*-phenyl-H). MALDI-TOF-MS (m/z): found 773.36 $[M^+]$, calcd., 773.14. **$CuTPP(NO_2)(CN)_2$**: MALDI-TOF-MS (m/z): 710.02 (calcd.,771.30). $C_{46}H_{25}N_7O_2Cu\cdot 0.5H_2O$: C, 70.81; H, 3.36; N, 12.57%. Found: C, 70.92; H, 3.50; N, 12.69%. **$CoTPP(NO_2)(CN)_2$**: MALDI-TOF-MS (m/z): found 766.19 $[M^+]$, calcd. 766.14. Anal. Calcd for $C_{46}H_{25}N_7O_2Co\cdot H_2O$: C, 70.41; H, 3.47; N, 12.50%. Found: C, 70.64; H, 3.25; N, 12.32%.

II. Synthesis of $MTPP(NO_2)X_6$ (X = Br, Ph, Th and PE) derivatives:

(a) Synthesis of 2-nitro-7,8,12,13,17,18-hexabromo-*meso*-tetraphenylporphyrinato Copper(II):[21c] $CuTPP(NO_2)$ (0.3 g, 0.416 mmol) was taken in 40 mL of distilled 1,2-dichloroethane in a 100 mL RB. To this, recrystallized NBS (0.74 g, 4.16 mmol) was added and refluxed for 16 hrs at 80℃. At the end of the reaction, the solvent was removed by rotary evaporation and redissolved in $CHCl_3$ (25 mL). The crude product was purified on silica column using $CHCl_3$ as eluent and recrystallised from $CHCl_3/CH_3OH$ mixture (1:3, v/v). The yield was found to be 0.28 g (81%).

MALDI-TOF-MS (m/z): found 1195.84 $[M+H]^+$, calcd. 1194.65. Anal. Calcd for $C_{44}H_{21}N_5Br_6O_2Cu\cdot 0.5H_2O$: C, 43.91; H, 1.84; N, 5.82%. Found: C, 43.76; H, 2.20; N, 5.28%.

(b) Synthesis of 2-nitro-7,8,12,13,17,18-hexabromo-*meso*-tetraphenylporphyrin and its metal complexes

$CuTPP(NO_2)Br_6$ (0.25 g, 0.209 mmol) was dissolved in 40 mL of $CHCl_3$. To this, 1.5 mL of conc. H_2SO_4 was added dropwise and stirred vigorously at 0°C for 1 hour. At the end of this period, distilled water (80 mL) was added dropwise to the reaction mixture with stirring. The organic layer was separated and washed with water (2 × 50 mL) followed by neutralization using aquous ammonia (25%) solution (20 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated to small volume. This was purified by silica gel chromatography using $CHCl_3$ as eluent, and the yield of the product was found to be 92%.

$H_2TPP(NO_2)Br_6$: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.59 (s, 1H, β-pyrrole-H), 8.24 (d, 4H, J = 7 Hz, *meso-o*-phenyl-H), 8.20 (ad, 4H, J = 7 Hz, *meso-o*-phenyl-H), 7.87-7.76 (m, 10H, J = 8.5 Hz, *meso-m*- and *p*-phenyl-H), 7.74 (t, 2H, J = 7.5 Hz, *meso-p*-phenyl-H). MALDI-TOF-MS (m/z): found 1133.51 $[M^+]$, calcd. 1133.12.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of MTPP(NO_2)Br_2 and the yields were found to 84 - 90%. **NiTPP(NO_2)Br_6:** ^{1}H NMR in $CDCl_3$: δ (ppm) 8.50 (s, 1H, β-pyrrole-H), 7.97 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.96-7.89 (m, 6H, *meso-o*-phenyl-H), 7.79-7.62 (m, 12H, *meso-m*- and *p*-phenyl-H). MALDI-TOF-MS (m/z): found 1190.12 [M^+], calcd. 1189.80. Anal. Calcd for $C_{44}H_{21}Br_6N_5O_2Ni$: C, 44.42; H, 1.78; N, 5.89%. Found: C, 44.12; H, 1.92; N, 5.66%. **ZnTPP(NO_2)Br_6:** ^{1}H NMR in $CDCl_3$: δ (ppm) 8.74 (s, 1H, β-pyrrole-H), 8.17 (t, 4H, J = 8 Hz, *meso-o*-phenyl-H), 8.11 (t, 4H, J = 8.5 Hz, *meso-o*-phenyl-H), 7.86-7.72 (m, 10H, *meso-m*- and *p*-phenyl-H), 7.69 (t, 2H, J = 7.5 Hz, *meso-p*-phenyl-H). MALDI-TOF-MS (m/z): found 1196.67 [M^+], calcd. 1196.50. **CoTPP(NO_2)Br_6:** MALDI-TOF-MS (m/z): found 1190.57 [M^+], calcd. 1190.04.

(b) Synthesis of 2-nitro-7,8,12,13,17,18-hexaphenyl-*meso*-tetraphenylporphyrin and its metal complexes:

H_2TPP(NO_2)Br_6 (0.3 g, 0.264 mmol), phenylboronic acid (0.774 g, 6.33 mmol) and K_2CO_3 (1.76 g, 12.67 mmol) were taken in a two-neck RB flask. To this, 120 mL of distilled toluene was added and purged with Ar gas for 15 minutes. Then Pd(PPh_3)$_4$ (0.061 g, 0.05 mmol) was added under Ar and heated to 100℃ for 15 hrs. After completion of the reaction, the solvent was removed by rotary evaporation. The crude porphyrin was redissolved in $CHCl_3$ (80 mL) and washed with saturated $NaHCO_3$ (70 mL) followed by 30% NaCl solution (50 mL). Finally, the organic layer was dried over anhydrous Na_2SO_4.The crude product was purified on silica column using variant polarity from $CHCl_3$ to 5 - 8% EtOAc in $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3$/CH_3OH mixture (1:3, v/v). The yield was found to be 0.23 g (78%).

H_2TPP(NO_2)Ph_6: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.31 (s, 1H, β-pyrrole-H), 8.03 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.85 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.58 (d, 2H, J = 7.5 Hz, *meso-o*-phenyl-H), 7.56 (d, 2H, J = 8 Hz, *meso-o*-phenyl-H), 7.39-7.18 (m, 5H, *meso-m*-phenyl-H), 6.96-6.58 (m, 33H, β-pyrrolePh-H, *meso-m*- and *p*-phenyl-H), 6.5 (d, 4H, J = 7 Hz, β-pyrrole Ph-H). ESI-MS (m/z): found 1176.38 [M•Na•K-H]$^+$, calcd. 1177.37. Anal. Calcd for $C_{80}H_{53}N_5O_2$: C, 86.07; H, 4.79; N, 6.27%. Found: C, 86.01; H, 4.93; N, 6.15%.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of MTPP(NO_2)Br_2 and crude products were purified by silica gel (for Co (II), Ni(II) and Cu(II)) or alumina for ZnTPP(NO_2)Ph_6 column chromatography using $CHCl_3$/5 - 6% EtOAc in $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3$/CH_3OH mixture (1:3, v/v) containing a drop of Et_3N. The yield was found to be 80-86%.

NiTPP(NO_2)Ph_6: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.37 (s, 1H, β-pyrrole-H), 7.60 (dd, 2H, J = 7Hz,J = 1 Hz, *meso-o*-phenyl-H), 7.57 (dd, 2H, J = 7Hz,J = 1 Hz, *meso-o*-phenyl-H), 7.25-7.12 (m, 4H, *meso-o*-phenyl-H), 7.06 (t, 2H, J = 7.5 Hz, *meso-m*-phenyl-H), 7.03 (t, 4H, J = 7.0 Hz, *meso-m*-phenyl-H), 6.88-6.50 (m, 36H, β-pyrrolePh-H, *meso-m*- and *p*-phenyl-H). MALDI-TOF-MS (m/z): found 1173.12 [M^+], calcd. 1173.01. **ZnTPP(NO_2)Ph_6:** ^{1}H NMR in $CDCl_3$: δ (ppm) 8.57 (s, 1H, β-pyrrole-H), 7.93 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.78 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.44 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.42 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.32-7.20 (m, 4H, J = 7.5 Hz, *meso-m*-phenyl-H), 7.16 (t, 2H, J = 8.0 Hz, *meso-m*-phenyl-H), 6.89-6.57 (m, 36H, β-pyrrolePh-H and *meso-m*- and *p*-phenyl-H). MALDI-TOF-MS (m/z): found 1179.62 [M^+], calcd. 1179.71. **CuTPP(NO_2)Ph_6:** MALDI-TOF-MS (m/z): found 1178.18

[M^+], calcd. 1177.86. Anal. Calcd for $C_{80}H_{51}N_5O_2Cu$: C, 78.13; H, 4.19; N, 5.66%. Found: C, 78.38; H, 4.30; N, 5.47%. **$CoTPP(NO_2)Ph_6$:** ESI-MS (m/z): found 1173.38 [M^+], calcd. 1173.25. Anal. Calcd for $C_{80}H_{51}N_5O_2Co$: C, 81.90; H, 4.38; N, 5.97%. Found: C, 81.98; H, 4.24; N, 5.74%.

(c) Synthesis of 2-nitro-7,8,12,13,17,18-hexaphenylethynyl-*meso*-tetraphenylporphyrin and its metal complexes

$H_2TPP(NO_2)Br_6$ (0.2 g, 0.176 mmol) and $Pd(PPh_3)_4$ (0.04 g, 0.035 mmol) were dissolved in distilled 1,4-dioxane and purged with Ar gas for 15 minutes. To this, tributyl(phenylethynyl)stannane (0.618 mL, 1.76 mmol) in 100 mL of degassed dioxane was added and heated to 80℃ for 40 minutes under Ar atmosphere. After completion of the reaction, the solvent was removed by vacuum distillation. The crude porphyrin was redissolved in $CHCl_3$ (20 mL) and purified on silica column using $CHCl_3$/hexane mixture (7:3, v/v) to 100% $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3/CH_3OH$ mixture (1:3, v/v) containing one drop of Et_3N. The yield was found to be 0.12 g (54%).

$H_2TPP(NO_2)(PE)_6$: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.60 (bs, 1H, β-pyrrole-H), 8.44 (d, 2H, J = 6.5 Hz, *meso-o*-phenyl-H), 8.40 (d, 2H, J = 7.5 Hz, *meso-o*-phenyl-H), 8.28 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.83-7.70 (m, 8H, *meso-m*-phenyl-H), 7.70-7.64 (m, 4H, *meso-p*-phenyl-H), 7.37-7.18 (m, 30H, β-pyrrole PE-H), -1.43 (bs, 2H, NH). ESI-MS (m/z): found 1261.47 [M+H]$^+$, calcd. 1261.47. Anal. Calcd for $C_{92}H_{53}N_5O_2 \cdot 1.5\ H_2O$: C, 85.83; H, 4.38; N, 5.44%. Found: C, 85.98; H, 4.33; N, 5.34%.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of $MTPP(NO_2)Br_2$ and the yields were found to be 80 - 90%. **$NiTPP(NO_2)(PE)_6$**: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.57 (s, 1H, β-pyrrole-H), 8.20 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 8.17 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 8.15-8.12 (m, 2H, *meso-o*-phenyl-H), 8.08 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.75-7.64 (m, 10H, *meso-m- and p*-phenyl-H), 7.62-7.54 (m, 2H, *meso-p*-phenyl-H), 7.32-7.16 (m, 30H, β-pyrrole PE-H). MALDI-TOF-MS (m/z): found 1317.63 [M^+], calcd. 1317.14. Anal. Calcd for $C_{92}H_{51}N_5O_2Ni$: C, 83.89; H, 3.90; N, 5.32%. Found: C, 83.53; H, 4.04; N, 5.19%. **$ZnTPP(NO_2)(PE)_6$**: ^{1}H NMR in $CDCl_3$: δ (ppm) 8.81 (s, 1H, β-pyrrole-H), 8.34 (d, 2H, J = 7.5 Hz, *meso-o*-phenyl-H), 8.32-8.29 (m, 4H, *meso-o*-phenyl-H), 8.22 (d, 2H, J = 8.5 Hz, *meso-o*-phenyl-H), 7.78-7.66 (m, 10H,*meso-m- and p*-phenyl-H), 7.62 (dt, 2H, J = 5 Hz, J = 2 Hz, *meso-p*-phenyl-H), 7.40-7.18 (m, 30H, β-pyrrole PE-H). MALDI-TOF-MS (m/z): found 1324.17 [M^+], calcd. 1323.84. **$CuTPP(NO_2)(PE)_6$**: MALDI-TOF-MS (m/z): found 1322.38 [M^+], calcd. 1322.00. Anal. Calcd for $C_{92}H_{51}N_5O_2Cu \cdot 1.5H_2O$: C, 81.97; H, 4.19; N, 5.11%. Found: C, 81.79; H, 3.96; N, 5.12%. **$CoTPP(NO_2)(PE)_6$**: ESI-MS (m/z): found 1317.41 [M^+], calcd. 1317.38. Anal. Calcd for $C_{92}H_{51}N_5O_2Co$: C, 83.88; H, 3.90; N, 5.31%. Found: C, 83.74; H, 3.73; N, 5.44%.

(d) Synthesis of 2-nitro-7,8,12,13,17,18-hexa(2-thienyl)-*meso*-tetraphenylporphyrin

$H_2TPP(NO_2)Br_6$ (0.070 g, 0.0617 mmol), thiophene-2-boronic acid (0.189 g, 1.477 mmol) and K_2CO_3 (0.252 g, 1.823 mmol) were taken in two-neck RB flask. To this, 35 mL of distilled toluene was added and purged with Ar gas for 15 minutes. Then $Pd(PPh_3)_4$(0.014 g, 0.012 mmol) was added under Ar and heated to 90℃ for 15 hrs. After completion of the reaction, the solvent

was removed by rotary evaporation. The crude porphyrin was redissolved in $CHCl_3$ (30 mL) and washed with saturated $NaHCO_3$ (25 mL) followed by 30% NaCl solution (25 mL). Finally, the organic layer was dried over anhydrous Na_2SO_4.The crude product was purified on silica column using variant polarity from $CHCl_3$ to 5-8% EtOAc in $CHCl_3$ as eluent. The desired product was recrystallised from $CHCl_3$/CH_3OH mixture (1:3, v/v). The yield was found to be 0.036 g (51%). $H_2TPP(NO_2)Th_6$: ^1H NMR in $CDCl_3$: δ (ppm) 8.28 (s, 1H, β-pyrrole-H), 7.82 (d, 1H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.98 (d, 1H, J = 6.5 Hz, *meso-o*-phenyl-H), 7.94 - 7.78 (m, 3H, *meso-o*-phenyl-H), 7.74 (s, 1H, *meso-o*-phenyl-H), 7.73 (s, 1H, *meso-o*-phenyl-H), 7.66 - 7.55 (m, 4H, *meso-o*-phenyl and *meso-m*-phenyl), 7.52 - 7.37 (m, 9H, *meso-m- and p*-phenyl), 7.37-7.27 (m, 2H, β-pyrroleTh-H), 7.15-6.96 (m, 6H, β-pyrroleTh-H), 6.95 - 6.84 (m, 2H, β-pyrroleTh-H), 6.80 - 6.25 (m, 8H, β-pyrroleTh-H). MALDI-TOF-MS (m/z): found 1152.21 [M^+], calcd. 1152.50. Anal. Calcd for $C_{68}H_{41}N_5O_2S_6$•0.5H_2O: C, 70.32; H, 3.64; N, 6.03; S, 16.56%. Found: C, 70.39; H, 3.80; N, 5.90; S, 16.55%.

The metal complexes were prepared with similar procedures of the corresponding metal complexes of $MTPP(NO_2)Br_2$ and the yields were found to be 80 - 90%. **$NiTPP(NO_2)Th_6$**: ^1H NMR in $CDCl_3$: δ (ppm) 8.39 (s, 1H, β-pyrrole-H), 7.82-7.63 (m, 6H, *meso-o*-phenyl-H), 7.41-7.28 (m, 8H, *meso-o- and m*-phenyl-H), 7.25-7.18 (m, 2H, *meso-m*-phenyl-H), 7.01-6.80 (m, 11H, *meso-p*-phenyl and β-pyrroleTh-H), 6.55- 6.17 (m, 11H, β-pyrroleTh-H). MALDI-TOF-MS (m/z): found 1209.50 [M^+], calcd. 1209.18. Anal. Calcd for $C_{68}H_{39}N_5O_2S_6Ni$•0.5H_2O: C, 64.84; H, 3.14; N, 5.52; S, 15.16%. Found: C, 64.69; H, 3.50; N, 5.20; S, 15.35%. **$ZnTPP(NO_2)Th_6$:** ^1H NMR in $CDCl_3$: δ (ppm) 8.50 (s, 1H, β-pyrrole-H), 8.09 (d, 2H, J = 7 Hz, *meso-o*-phenyl-H), 7.97 (d, 2H, J = 6.5 Hz, *meso-m*-phenyl-H), 7.84 - 7.73 (m, 4H, *meso-o*-phenyl-H), 7.44 - 7.28 (m, 6H, *meso-m*-phenyl), 7.08 - 6.89 (m, 8H, *meso-m*- and *p*-phenyl, β-pyrroleTh-H), 6.88 - 6.75 (m, 4H, β-pyrroleTh-H), 6.65 - 6.29 (m, 12H, β-pyrroleTh-H). MALDI-TOF-MS (m/z): found 1216.36 [M^+], calcd. 1215.88. **$CuTPP(NO_2)Th_6$:** MALDI-TOF-MS (m/z): found 1214.49 [M^+], calcd. 1214.03. Anal. Calcd for $C_{68}H_{39}N_5O_2S_6Cu$: C, 64.84; H, 3.24; N, 5.77; S, 15.85%. Found: C, 64.65; H, 3.50; N, 5.89; S, 15.67%. **$CoTPP(NO_2)Th_6$:** ESI-MS (m/z): found 1208.11 [M^+], calcd. 1208.08. Anal. Calcd for $C_{68}H_{39}N_5O_2S_6Co$: C, 67.53; H, 3.25; N, 5.79; S, 15.91%. Found: C, 67.74; H, 3.42; N, 5.81; S, 15.45%.

Fig. S1. The ORTEP diagrams showing top and side views of $NiTPP(NO_2)(Th)_2(Py)$ (1a and 1b), $ZnTPP(NO_2)(PE)_2(CH_3OH)$ (1d and 1e) and $ZnTPP(NO_2)Br_2(CH_3OH)$ (1g and 1h). The solvates are not shown for clarity, and in side view, the β-substituents and *meso*-phenyl groups are not shown for clarity. The displacement of porphyrin-core atoms in Å from the mean plane are shown in figures 1c, 1f and 1i for $NiTPP(NO_2)(Th)_2(Py)$, $ZnTPP(NO_2)(PE)_2(CH_3OH)$ and $ZnTPP(NO_2)Br_2$, respectively.

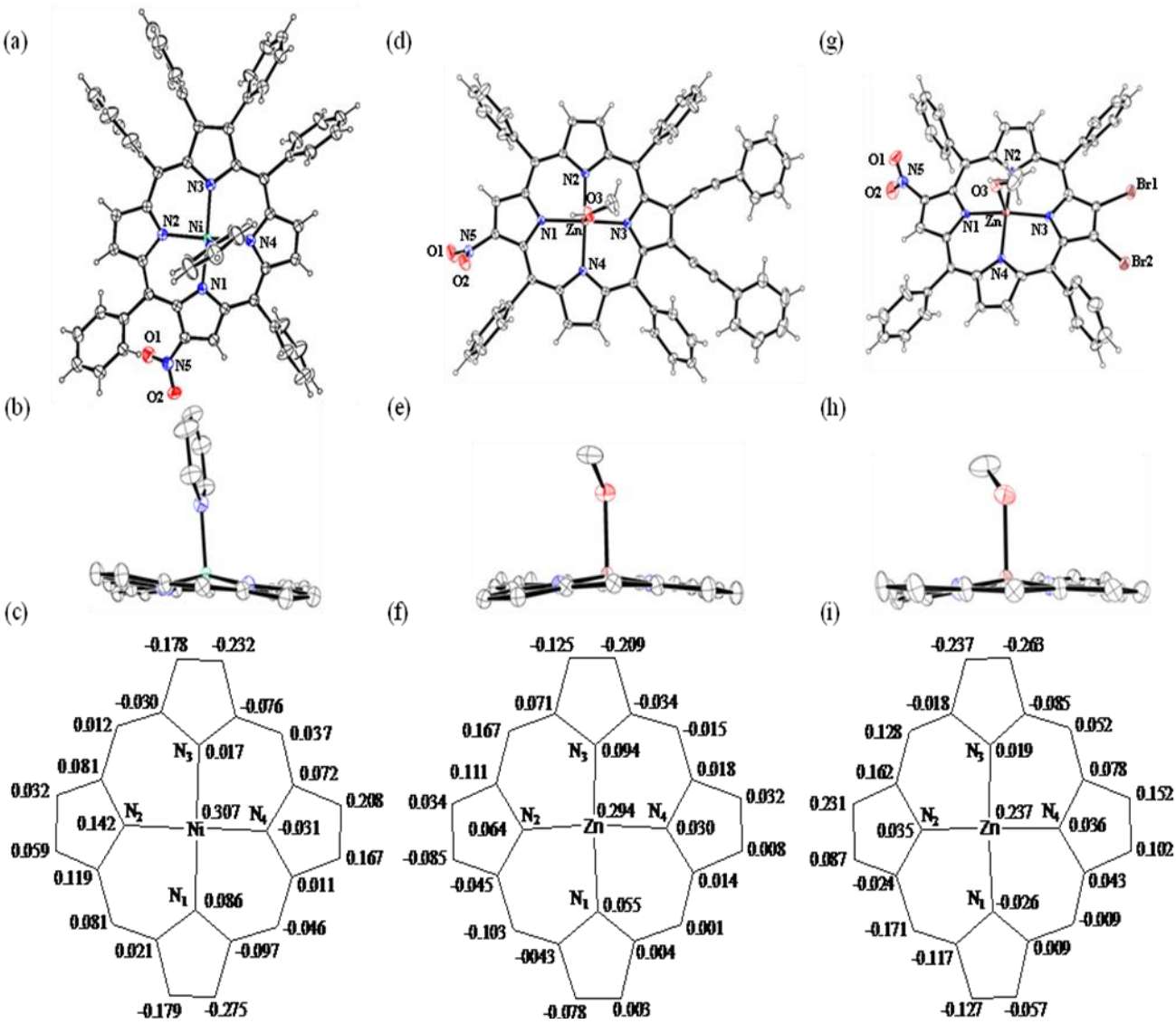
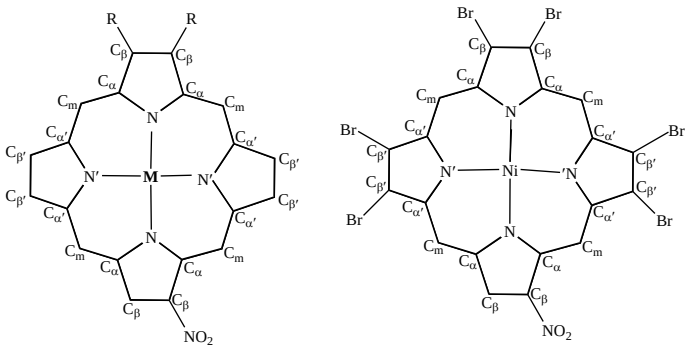


Table S1. Crystal structure data of $NiTPP(NO_2)(Ph)_2(Pyridine)$ (**1**), $ZnTPP(NO_2)(PE)_2(CH_3OH)$ (**2**), $ZnTPP(NO_2)Br_2(CH_3OH)$ (**3**), $NiTPP(NO_2)Br_6$ (**4**), and $H_2TPP(NO_2)(Th)_2$ (**5**).

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{61}H_{40}N_6O_2Ni$	$C_{61}H_{43}N_5O_4Zn$	$C_{45}H_{29}N_5O_5Br_2Zn$	$C_{88}H_{42}N_{10}O_4Br_{12}Ni_2$	$C_{53}H_{39}C_{l0}N_5O_4S_2$
Formula wt.	947.70	975.37	944.90	2379.66	874.01
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	P-1	P-1	P-1	P-1
a (Å)	11.938(5)	12.7702(6)	12.490(1)	14.211(5)	13.948(5)
b (Å)	12.248(5)	13.5976(6)	13.544(2)	14.367(5)	14.270(5)
c (Å)	17.642(5)	16.1781(7)	14.381(2)	19.651(5)	14.559(5)
α (º)	109.644(5)	66.257(2)	107.593(7)	89.091(5)	118.629(5)
β (º)	99.080(5)	79.410(2)	108.531(7)	89.869(5)	94.368(5)
γ (º)	94.664(5)	75.696(2)	103.813(8)	89.984(5)	112.334(5)
Volume ($Å^3$)	2373.8(15)	2480.46(19)	2042.3(5)	4012(2)	2230.5(14)
Z	2	2	2	2	2
D_{cald} (mg/m^3)	1.326	1.306	1.537	1.970	1.301
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (˚C)	293 K	293 K	293 K	293 K	293 K
No. of total reflns.	11581	12091	30281	16103	11007
No. of indepnt. reflns.	6207	8376	9620	9459	4083
R^a	0.0615	0.0625	0.1061	0.0585	0.1083
$R_w{}^b$	0.1337	0.1886	0.2598	0.1562	0.2415
CCDC	1018319	1018393	1019075	1019824	1018509

Table S2. Selected bond lengths and bond angles of $NiTPP(NO_2)Ph_2(Py)$ (**1**), $ZnTPP(NO_2)(PE)_2(MeOH)$ (**2**), $ZnTPP(NO_2)Br_2(MeOH)$ (**3**), $NiTPP(NO_2)Br_6$ (**4**) and $H_2TPP(NO_2)(Th)_2$ (**5**).



	1	**2**	**3**	**4**	**5**
	Bond Length (Å)				
M-N	**2.112(3)**	**2.088(2)**	**2.087(9)**	**1.920(6)**	-
M-N′	2.048(3)	2.042(3)	2.042(9)	1.927(6)	-
M-O/M-N	2.156(3)	2.173(3)	2.154(12)	-	-
N-C_α	1.377(4)	1.372(4)	1.370(13)	1.384(10)	1.368(7)
N′-C_α	1.376(4)	1.372(4)	1.349(13)	1.375(10)	1.376(6)
C_α-C_β	1.450(5)	1.448(4)	1.453(15)	1.447(10)	1.460(7)
$C_{\alpha'}$-$C_{\beta'}$	1.439(5)	1.445(5)	1.468(15)	1.443(10)	1.422(9)
C_β-C_β	**1.349(5)**	**1.370(5)**	**1.334(15)**	**1.336(10)**	**1.340(9)**
$C_{\beta'}$-$C_{\beta'}$	1.344(5)	1.339(5)	1.298(15)	**1.349(10)**	1.358(6)
C_α-C_m	1.394(4)	1.402(4)	1.404(15)	1.392(10)	1.408(9)
$C_{\alpha'}$-C_m	1.404(5)	1.403(4)	1.406(15)	1.399(10)	1.399(6)
ΔC_β (Å)[a]	**0.166**	**0.072**	**0.157**	**1.10**	**0.750**
Δ24 (Å)[b]	**0.095**	**0.061**	**0.095**	**0.564**	**0.367**
ΔMetal (Å)	**0.397**	**0.295**	**0.237**	**0.035**	-
	Bond Angle (deg)				
M-N-C_α	**126.2(2)**	**126.0(2)**	**125.9(8)**	**125.4(5)**	-
M-N′-C_α	125.9(2)	126.4(2)	125.7(8)	**125.0(5)**	-
N-M-N	160.7(1)	167.9(1)	166.7(4)	169.8(3)	-
N′-M-N′	161.1(1)	166.1(1)	168.7(4)	170.2(2)	-
N-C_α-C_m	**125.0(3)**	**125.2(3)**	**125.4(10)**	**123.3(7)**	**124.1(5)**
N′-$C_{\alpha'}$-C_m	126.4(3)	126.6(3)	127.6(10)	**122.9(7)**	125.9(5)
N-C_α-C_β	108.8(3)	108.9(3)	108.2(10)	109.0(6)	109.7(5)
N′-$C_{\alpha'}$-$C_{\beta'}$	109.5(3)	109.2(3)	108.6(10)	108.9(6)	106.0(5)
C_β- C_α-C_m	**126.1(3)**	**125.5(3)**	**126.3(10)**	**127.2(7)**	**125.9(5)**
$C_{\beta'}$- $C_{\alpha'}$-C_m	124.0(3)	124.2(3)	123.8(10)	**127.2(7)**	128.1(5)
C_α-C_m-$C_{\alpha'}$	125.2(3)	125.0(3)	124.3(10)	120.3(7)	124.2(5)
C_α-C_β-C_β	107.5(3)	107.0(3)	107.7(10)	107.7(7)	106.9(5)
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	107.4(3)	107.4(3)	107.5(11)	107.3(7)	108.6(6)
C_α-N-C_α	107.5(3)	107.9(2)	108.0(9)	106.2(6)	106.3(4)
$C_{\alpha'}$-N- $C_{\alpha'}$	106.3(3)	106.8(2)	107.8(9)	106.8(6)	110.8(4)

[a] ΔC_β refers to the mean plane displacement of the β-pyrrole carbons
[b] Δ24 refers to the mean plane deviation of 24-atom core

Figure S2. B3LYP/LanLD2Z optimised geometries showing top as well as side views of **H_2TPP(NO_2)($CN)_2$** (**1a** and **1b**) and **H_2TPP(NO_2)($PE)_2$** (**1d** and **1e**), respectively. In side view, the β-substituents and *meso*-phenyl groups are not shown for clarity. The displacement of porphyrin-core atoms in Å from the mean plane are shown in figures **1c** and **1f** for **H_2TPP(NO_2)($CN)_2$** and **H_2TPP(NO_2)($PE)_2$**, respectively. Color codes for atoms: C (black), N (blue) and O (red).

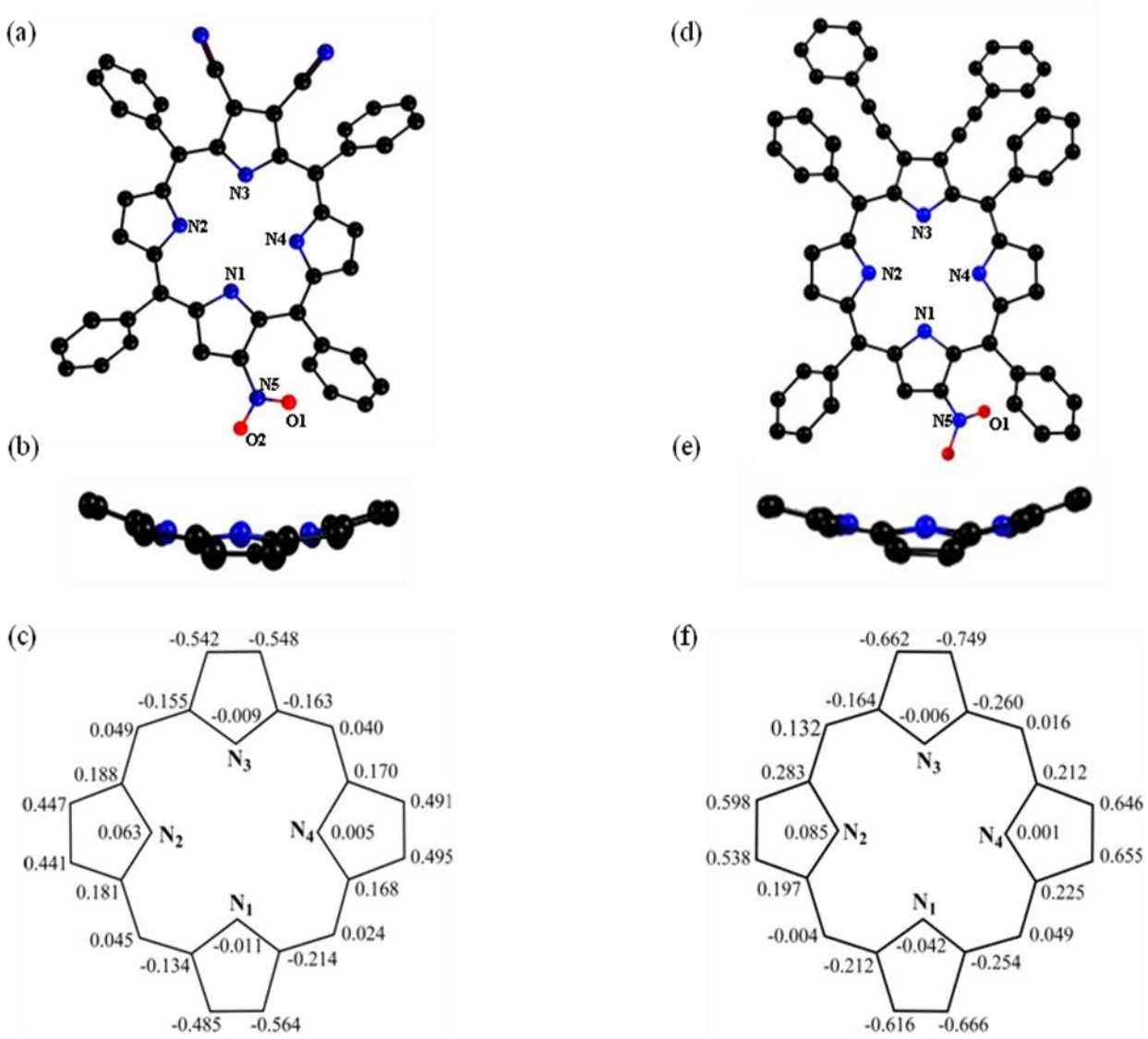


Figure S3. B3LYP/LanLD2Z optimised geometries showing top as well as side views of **H_2TPP(NO_2)Ph_2** (**1a** and **1b**) and **H_2TPP(NO_2)Br_2** (**1d** and **1e**), respectively. In side view, the β-substituents and *meso*-phenyl groups are not shown for clarity. The displacement of porphyrin-core atoms in Å from the mean plane are shown in figures **1c** and **1f** for **H_2TPP(NO_2)Ph_2** and **H_2TPP(NO_2)Br_2**, respectively. Color codes for atoms: C (black), N (blue), O (red) and Br (brown).

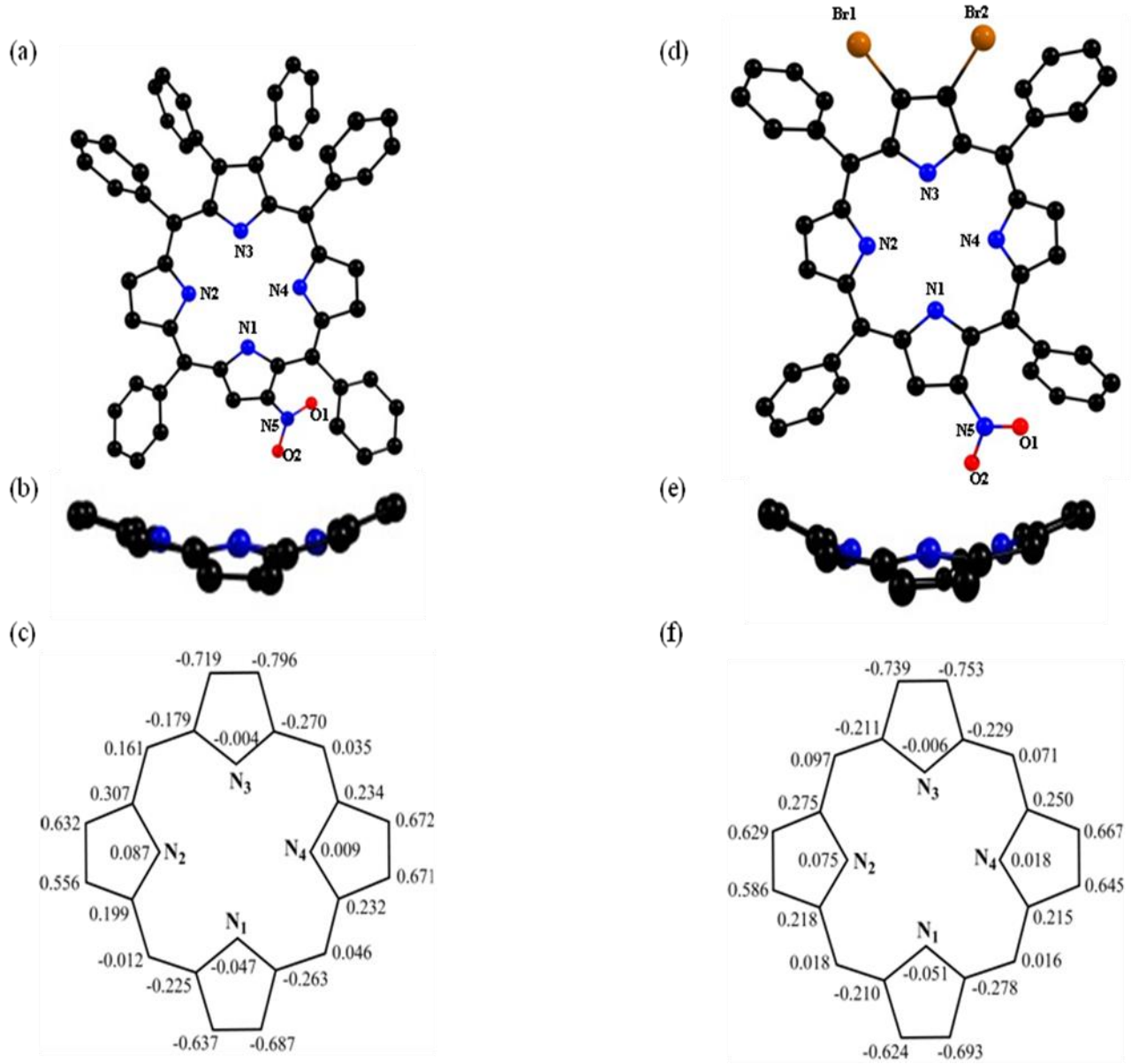


Figure S4. B3LYP/LanLD2Z optimised geometries showing top as well as side views of **H_2TPP(NO_2)(PE)$_6$** (**1a** and **1b**) and **H_2TPP(NO_2)Ph_6** (**1d** and **1e**), respectively. In side view, the β-substituents and *meso*-phenyl groups are not shown for clarity. The displacement of porphyrin-core atoms in Å from the mean plane are shown in figures **1c** and **1f** for **H_2TPP(NO_2)(PE)$_6$** and **H_2TPP(NO_2)Ph_6**, respectively. Color codes for atoms: C (black), N (blue) and O (red).

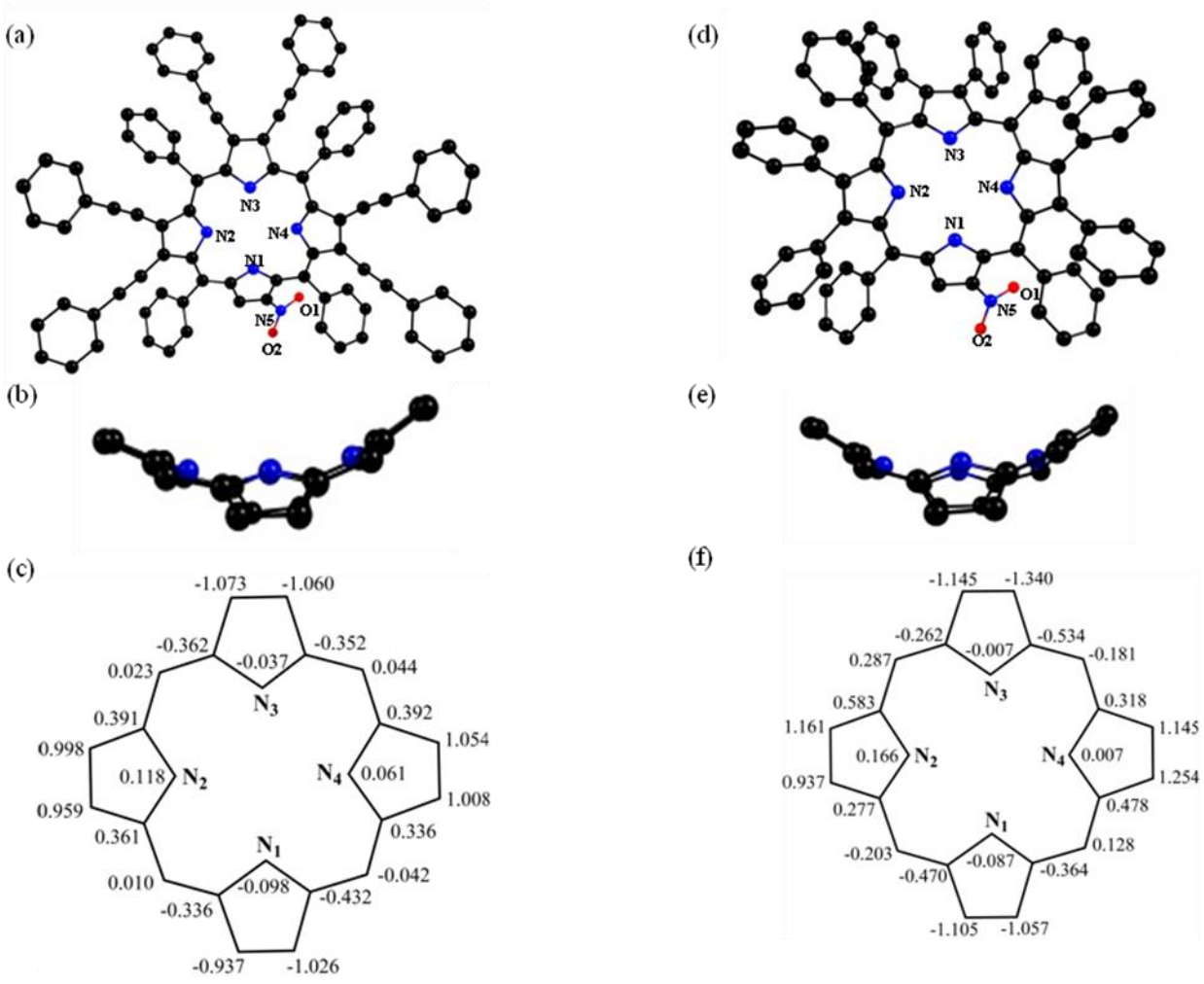
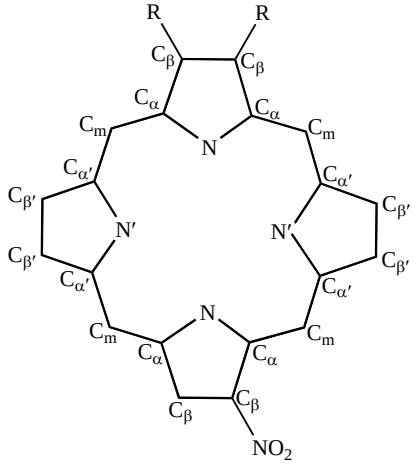


Table S3. Selected bond lengths (Å) and bond angles (º) for the B3LYP/LanLD2Z optimised geometries of $H_2TPP(NO_2)X_2$ (X = CN, PE, Br, Ph and Th).

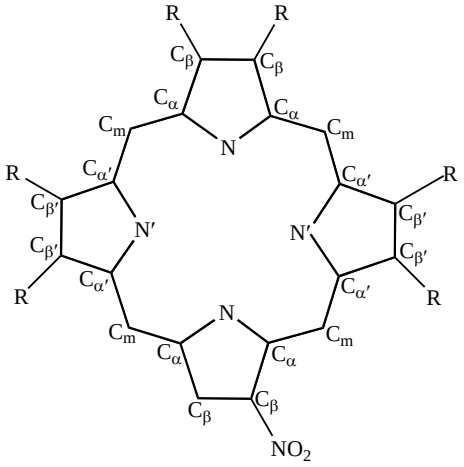


R = CN, PE, Br, Ph and **Th**

	$H_2TPP(NO_2)(CN)_2$	**$H_2TPP(NO_2)(PE)_2$**	**$H_2TPP(NO_2)Br_2$**	**$H_2TPP(NO_2)(Ph)_2$**	**$H_2TPP(NO_2)(Th)_2$**
Bond Length (Å)					
N-C_α	1.386	1.387	1.389	1.388	1.387
N′-C_α	1.392	1.393	1.392	1.392	1.392
C_α-C_β	1.467	1.471	1.460	1.472	1.471
$C_{\alpha'}$-$C_{\beta'}$	1.447	1.447	1.394	1.447	1.447
C_β-C_β	1.382	1.390	1.375	1.380	1.384
$C_{\beta'}$-$C_{\beta'}$	1.380	1.380	1.380	1.381	1.381
C_α-C_m	1.423	1.423	1.420	1.424	1.425
$C_{\alpha'}$-C_m	1.411	1.413	1.413	1.412	1.413
ΔC_β (Å)[a]	**0.501**	**0.641**	**0.667**	**0.671**	**0.727**
Δ24 (Å)[b]	**0.234**	**0.294**	**0.315**	**0.320**	**0.344**
Bond Angle (deg)					
N-C_α-C_m	**125.7**	**124.7**	**124.7**	**124.6**	**124.5**
N′-$C_{\alpha'}$-C_m	127.2	127.1	127.0	126.7	126.6
N-C_α-C_β	109.5	109.8	109.2	109.9	109.9
N′-$C_{\alpha'}$-$C_{\beta'}$	106.5	106.4	106.4	106.4	106.3
C_β- C_α-C_m	**124.7**	**125.3**	**125.9**	**125.3**	**125.4**
$C_{\beta'}$- $C_{\alpha'}$-C_m	126.3	126.5	126.6	126.9	127.1
C_α-C_m-$C_{\alpha'}$	124.0	123.9	123.8	123.8	123.5
C_α-C_β-C_β	106.8	106.6	107.0	106.6	106.6
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	108.3	108.3	108.2	108.2	108.3
C_α-N-C_α	107.1	106.9	107.2	106.5	106.7
$C_{\alpha'}$-N- $C_{\alpha'}$	110.4	110.5	110.6	110.6	110.6

[a] ΔC_β refers to the mean plane displacement of the β-pyrrole carbons
[b] Δ24 refers to the mean plane deviation of 24-atom core

Table S4. Selected bond lengths (Å) and bond angles (º) for the B3LYP/LanLD2Z optimised geometries of $H_2TPP(NO_2)X_6$ (X = PE, Br, Ph and Th).



R = PE, Br, Ph and **Th**

	$H_2TPP(NO_2)(PE)_6$	**$H_2TPP(NO_2)Br_6$**	**$H_2TPP(NO_2)Ph_6$**	**$H_2TPP(NO_2)(Th)_6$**
	Bond Length (Å)			
N-C_α	1.387	1.388	1.386	1.385
N′-C_α	1.389	1.391	1.387	1.386
C_α-C_β	1.470	1.470	1.473	1.473
$C_{\alpha'}$-$C_{\beta'}$	1.453	1.451	1.457	1.456
C_β-C_β	1.388	1.375	1.382	1.385
$C_{\beta'}$-$C_{\beta'}$	1.417	1.391	1.404	1.410
C_α-C_m	1.425	1.425	1.427	1.428
$C_{\alpha'}$-C_m	1.415	1.419	1.419	1.421
ΔC_β (Å)	**1.014**	**1.152**	**1.143**	**1.240**
Δ24 (Å)	**0.479**	**0.542**	**0.562**	**0.581**
	Bond Angle (deg)			
N-C_α-C_m	**124.6**	**124.0**	**123.8**	**123.4**
N′-$C_{\alpha'}$-C_m	**124.5**	**123.8**	**123.2**	**123.1**
N-C_α-C_β	109.7	109.2	109.8	109.6
N′-$C_{\alpha'}$-$C_{\beta'}$	106.1	105.2	106.3	106.2
C_β- C_α-C_m	**125.5**	**126.5**	**126.2**	**126.7**
$C_{\beta'}$- $C_{\alpha'}$-C_m	**129.2**	**130.8**	**130.3**	**130.6**
C_α-C_m-$C_{\alpha'}$	123.0	122.2	122.3	121.7
C_α-C_β-C_β	106.1	107.0	106.6	106.6
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	107.7	108.4	107.8	107.7
C_α-N-C_α	107.0	107.3	106.8	107.8
$C_{\alpha'}$-N- $C_{\alpha'}$	111.9	112.2	111.5	111.8

[a] ΔC_β refers to the mean plane displacement of the β-pyrrole carbons
[b] Δ24 refers to the mean plane deviation of 24-atom core

Table S5. Optical absorption spectral data of metal complexes of mixed substituted porphyrins

Porphyrin	**B band(s), nm**	**Q band(s), nm**
$CoTPP(NO_2)$	382(sh), 420(5.08)	540(4.03), 578(3.94)
$CoTPP(NO_2)Br_2$	383(sh), 431(5.04)	551(3.94), 595(4.02)
$CoTPP(NO_2)Ph_2$	388(sh), 434(4.98)	553(3.96), 593(3.98)
$CoTPP(NO_2)(PE)_2$	441(5.16)	609(4.30)
$CoTPP(NO_2)Th_2$	435(5.07)	602(4.13)
$CoTPP(NO_2)(CN)_2$	431(5.18)	609(4.39)
$CoTPP(NO_2)Br_6$	453(5.11)	567(4.07)
$CoTPP(NO_2)Ph_6$	400(sh), 454(5.01)	570(4.00), 611(3.96)
$CoTPP(NO_2)(PE)_6$	487(5.29)	597(4.39)
$CoTPP(NO_2)Th_6$	464(5.00)	580(4.13), 627(3.96)
$NiTPP(NO_2)$	386(sh), 428(5.14)	539(4.07), 583(3.97)
$NiTPP(NO_2)Br_2$	385(sh), 437(5.17)	548(4.02), 597(4.11)
$NiTPP(NO_2)Ph_2$	389(sh), 440(5.10)	550(4.04), 598(4.07)
$NiTPP(NO_2)(PE)_2$	446(5.23)	561(4.06), 614(4.94)
$NiTPP(NO_2)Th_2$	323(4.26), 441(5.12)	555(4.03), 605(4.17)
$NiTPP(NO_2)(CN)_2$	435(5.25)	612(4.47)
$NiTPP(NO_2)Br_6$	348(4.36), 454(5.22)	565(4.16), 603(3.90)
$NiTPP(NO_2)Ph_6$	456(5.04)	569(4.03), 621(3.99)
$NiTPP(NO_2)(PE)_6$	489(5.30)	598(4.43), 638(4.16)
$NiTPP(NO_2)Th_6$	466(5.09)	580(4.17), 631(4.09)
$CuTPP(NO_2)$	380(sh), 422(5.26)	547(4.15), 589(3.96)
$CuTPP(NO_2)Br_2$	430(5.23)	556(4.02), 600(4.05)
$CuTPP(NO_2)Ph_2$	384(sh), 432(5.18)	556(4.06), 601(4.00)
$CuTPP(NO_2)(PE)_2$	442(5.28)	565(4.05), 613(4.30)
$CuTPP(NO_2)Th_2$	433(5.23)	561(4.07), 608(4.14)

$CuTPP(NO_2)(CN)_2$	434(5.41)	571(3.99), 618(4.58)
$CuTPP(NO_2)Br_6$	361(4.34), 461(5.01)	584(4.07), 625(3.80)
$CuTPP(NO_2)Ph_6$	450(5.01)	582(4.02), 630(3.90)
$CuTPP(NO_2)(PE)_6$	493(5.28)	610(4.43)
$CuTPP(NO_2)Th_6$	460(4.81)	596(3.93), 639(3.72)
$ZnTPP(NO_2)$	426(5.23)	556(4.07), 599(3.90)
$ZnTPP(NO_2)Br_2$	340(4.29), 433(5.36)	562(4.12), 606(4.10)
$ZnTPP(NO_2)Ph_2$	435(5.27)	561(4.12), 607(4.00)
$ZnTPP(NO_2)(PE)_2$	446(5.38)	573(4.16), 620(4.35)
$ZnTPP(NO_2)Th_2$	437(5.25)	564(4.07), 612(4.08)
$ZnTPP(NO_2)(CN)_2$	442(5.42)	634(4.47)
$ZnTPP(NO_2)Br_6$	377(4.38), 476(5.00)	600(sh), 682(4.11)
$ZnTPP(NO_2)Ph_6$	379(4.37), 467(5.07)	595(3.90), 648(3.86)
$ZnTPP(NO_2)(PE)_6$	494(5.35)	613(4.35), 696(sh)
$ZnTPP(NO_2)Th_6$	476(5.06)	607(4.01), 663(3.92)

Values in parentheses refer to log ε (ε in Mol^{-1} cm^{-1}).

Table S6. Fluorescence Spectral data of mixed substituted porphyrins in CH_2Cl_2 at 298 K.

Porphyrin	λ_{Ex}nm	$\lambda_{fl,max}$nm	Quantum Yield, ϕ_f	Stoke shift (nm)	Stokes shift (cm^{-1})
$H_2TPP(NO_2)Ph_2$	439	756	0.0167	70	1350
$H_2TPP(NO_2)(PE)_2$	444	746	0.0180	59	1151
$H_2TPP(NO_2)Th_2$	440	768, 805(sh)	0.0092	73	1367
$H_2TPP(NO_2)(CN)_2$	440	728	0.0582	26	509
$H_2TPP(NO_2)(PE)_6$	494	813	0.0023	62	1016
$ZnTPP(NO_2)Ph_2$	435	709	0.0110	102	2370
$ZnTPP(NO_2)(PE)_2$	446	687	0.0160	67	1573
$ZnTPP(NO_2)Th_2$	437	712	0.0100	100	2295
$ZnTPP(NO_2)(CN)_2$	442	662	0.0334	28	667
$ZnTPP(NO_2)(PE)_6$	494	737	0.0051	41	799

Figure S5. Electronic absorption spectra of $H_2TPP(NO_2)X_2$ (X = H, CN, PE) derivatives in CH_2Cl_2 at 298 K. Q bands are magnified 3 times.

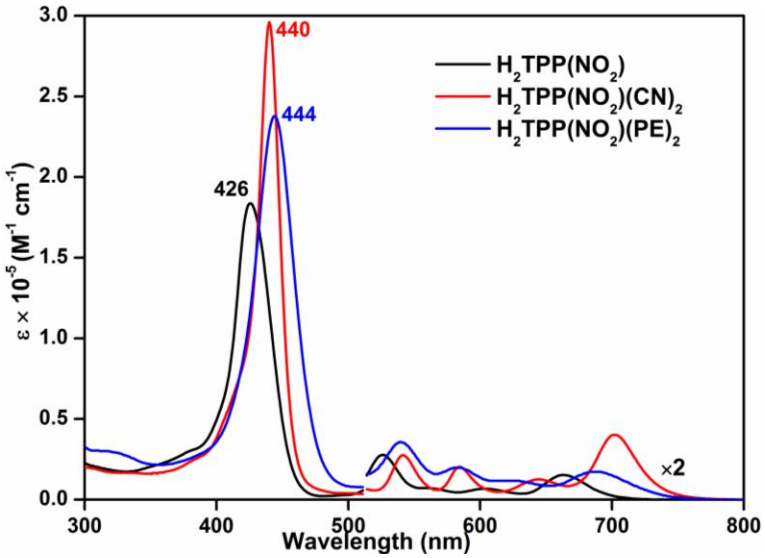


Figure S6. UV- Visible spectra of $H_2TPP(NO_2)X_6$ (X = H, Ph, Th, PE) derivatives in CH_2Cl_2 at 298 K. Q bands are magnified 3 times.

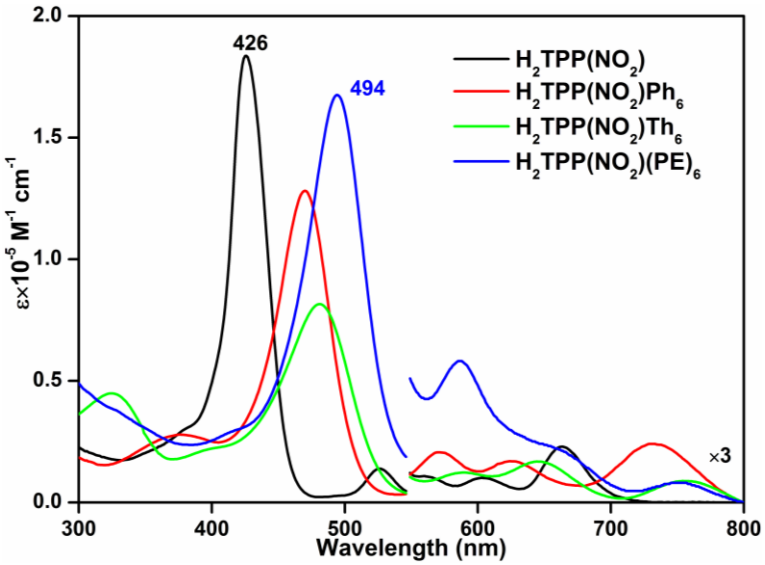


Figure S7.Fluorescence spectra of $H_2TPP(NO_2)Th_n$ (n = 0, 2, 6) in CH_2Cl_2 at 298 K.

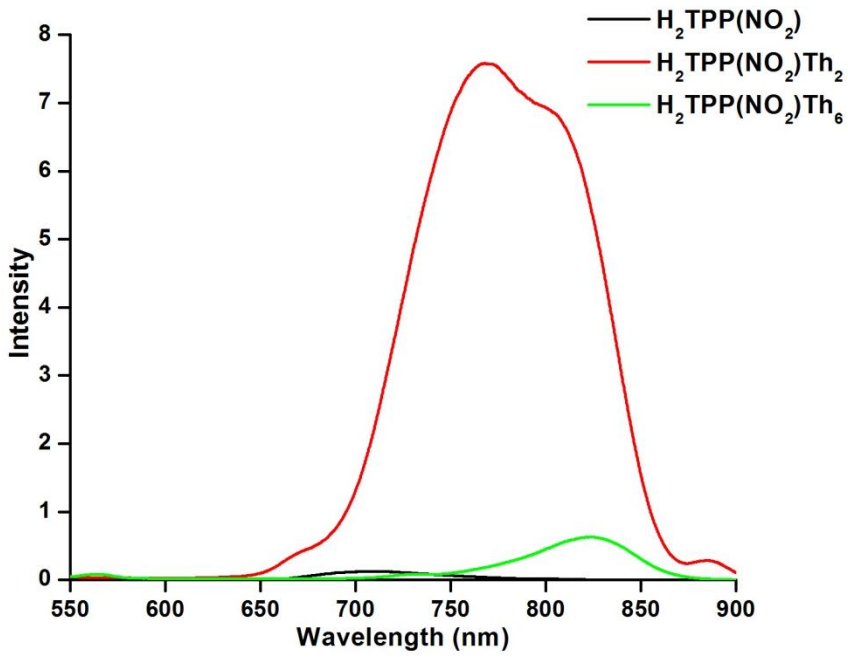


Figure S8. Emission spectra of (a) $MTPP(NO_2)(CN)_2$ and (b) $MTPP(NO_2)(C_6H_5)_2$, where M = 2H and Zn(II) in CH_2Cl_2 at 298 K.

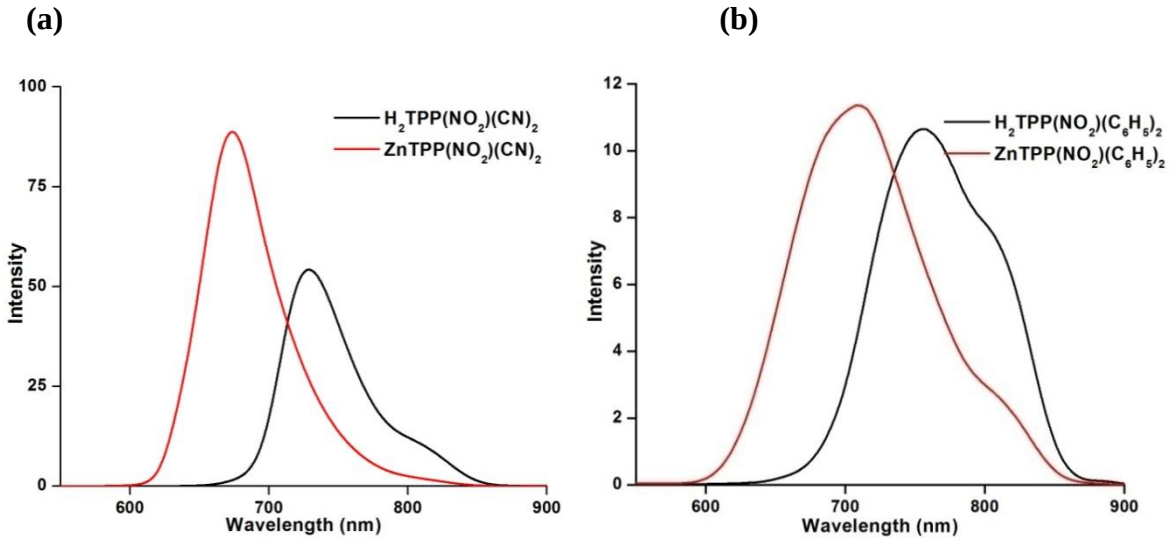


Figure S9. Fluorescence spectra of (a) $MTPP(NO_2)(PE)_2$ and (b) $MTPP(NO_2)(PE)_6$ (M = 2H, Zn(II)) in CH_2Cl_2 at 298 K.

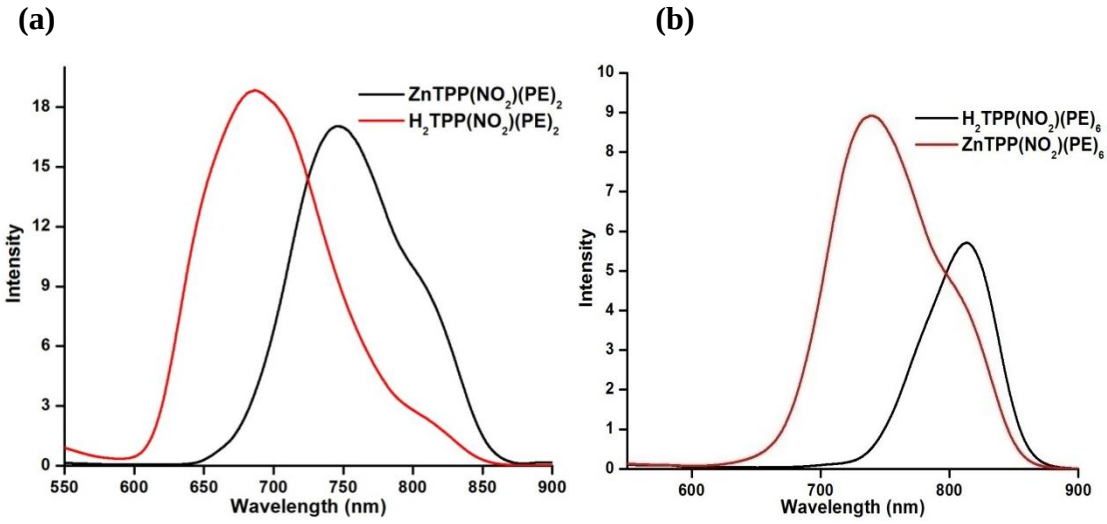


Figure S10.[1]H NMR spectrum of $H_2TPP(NO_2)Br_2$ in $CDCl_3$at 298 K.

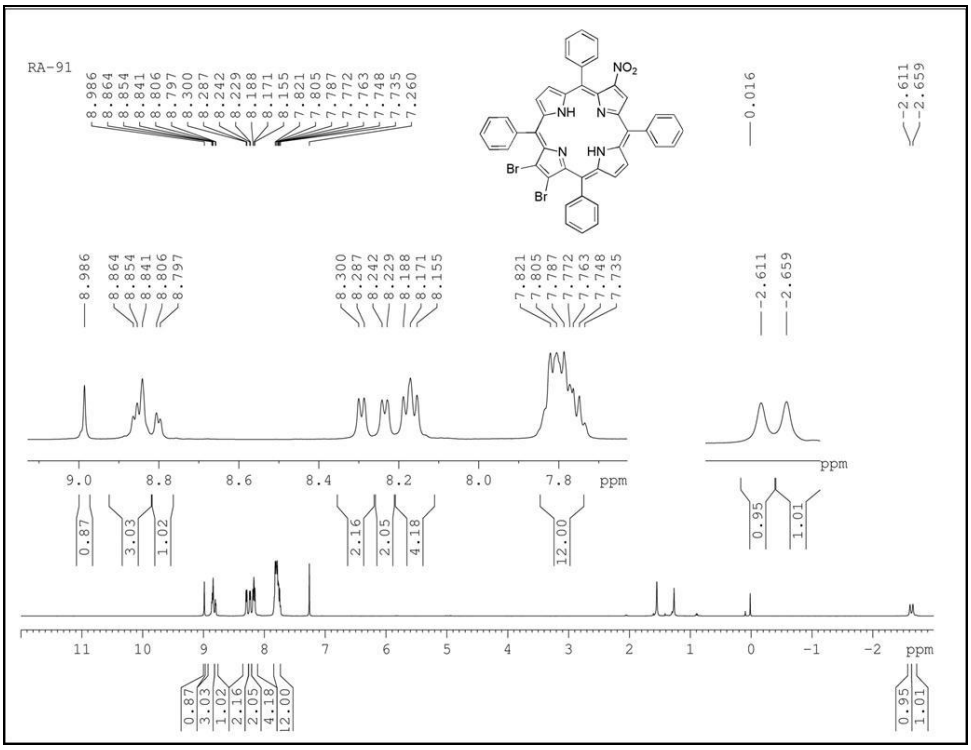


Figure S11. [1]H NMR spectrum of $NiTPP(NO_2)Br_2$ in $CDCl_3$.

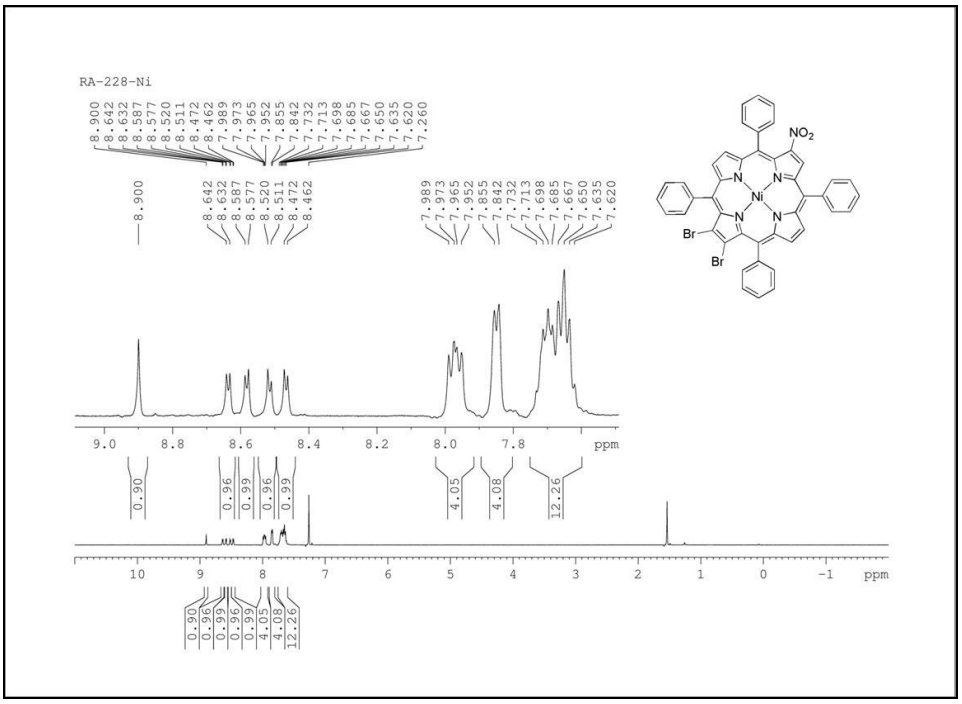


Figure S12. ^{1}H NMR spectrum of $ZnTPP(NO_2)Br_2$ in $CDCl_3$.

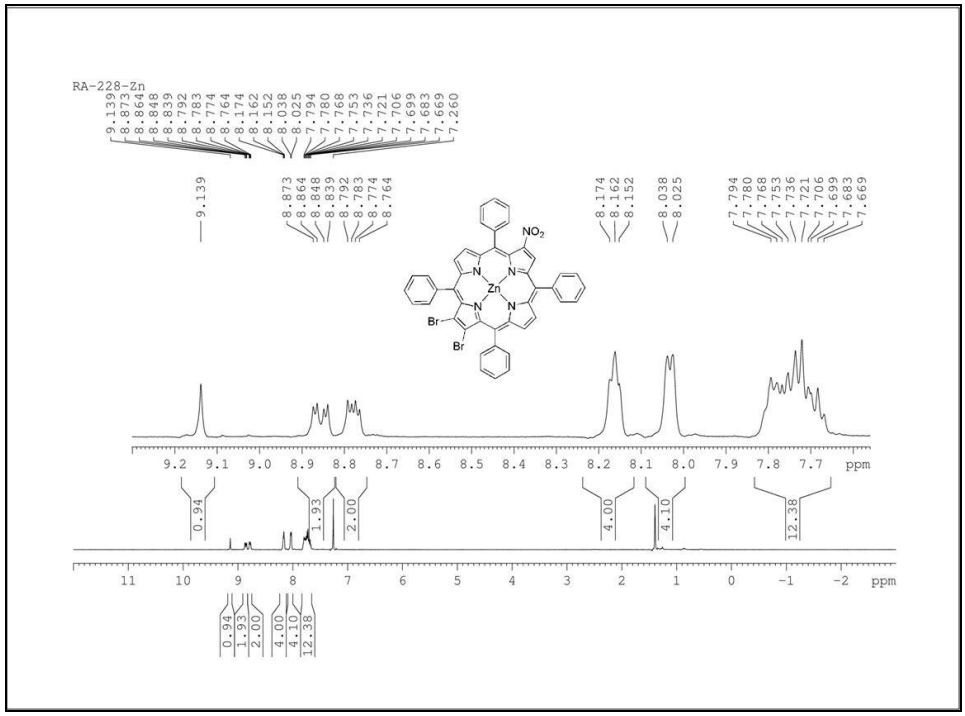


Figure S13. ^{1}H NMR spectrum of $H_2TPP(NO_2)Ph_2$ in $CDCl_3$.

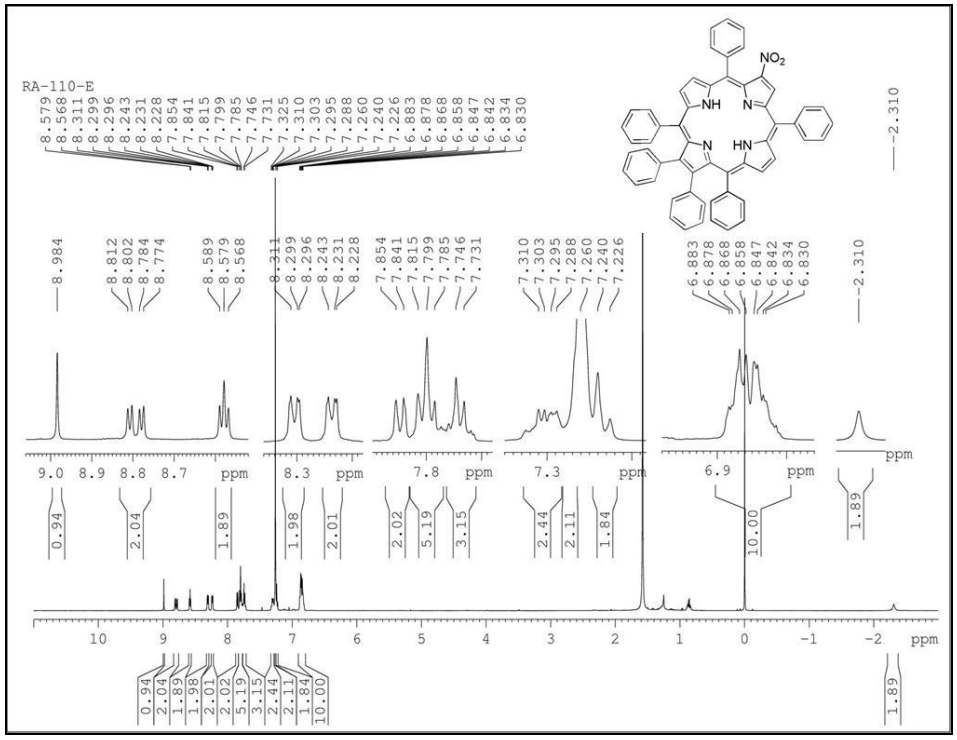


Figure S14. ^{1}H NMR spectrum of NiTPP(NO_2)Ph_2 in $CDCl_3$.

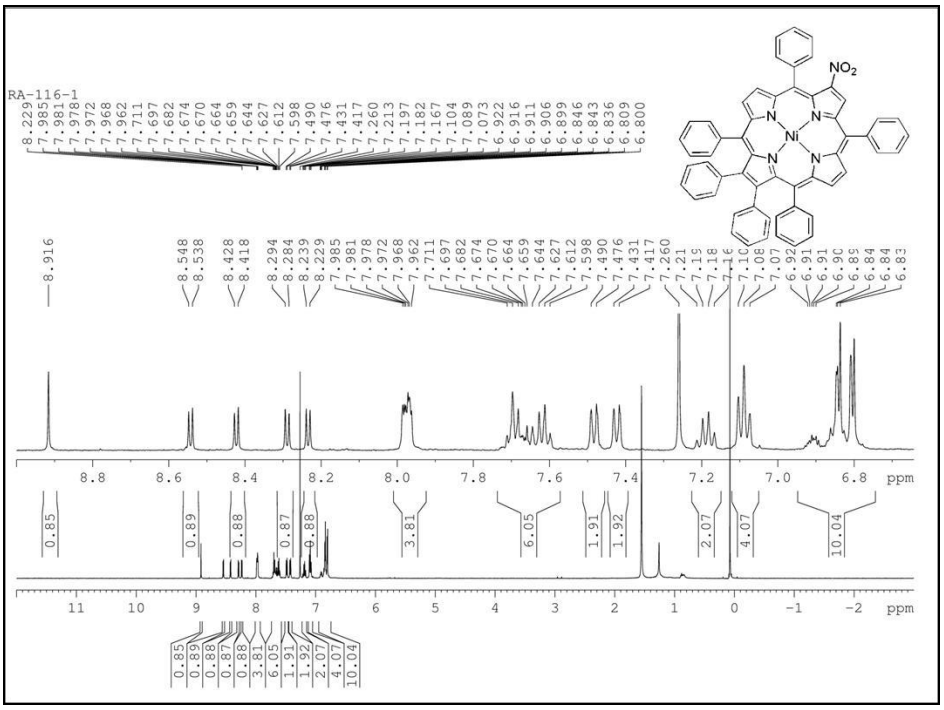


Figure S15. ^{1}H NMR spectrum of ZnTPP(NO_2)Ph_2 in $CDCl_3$.

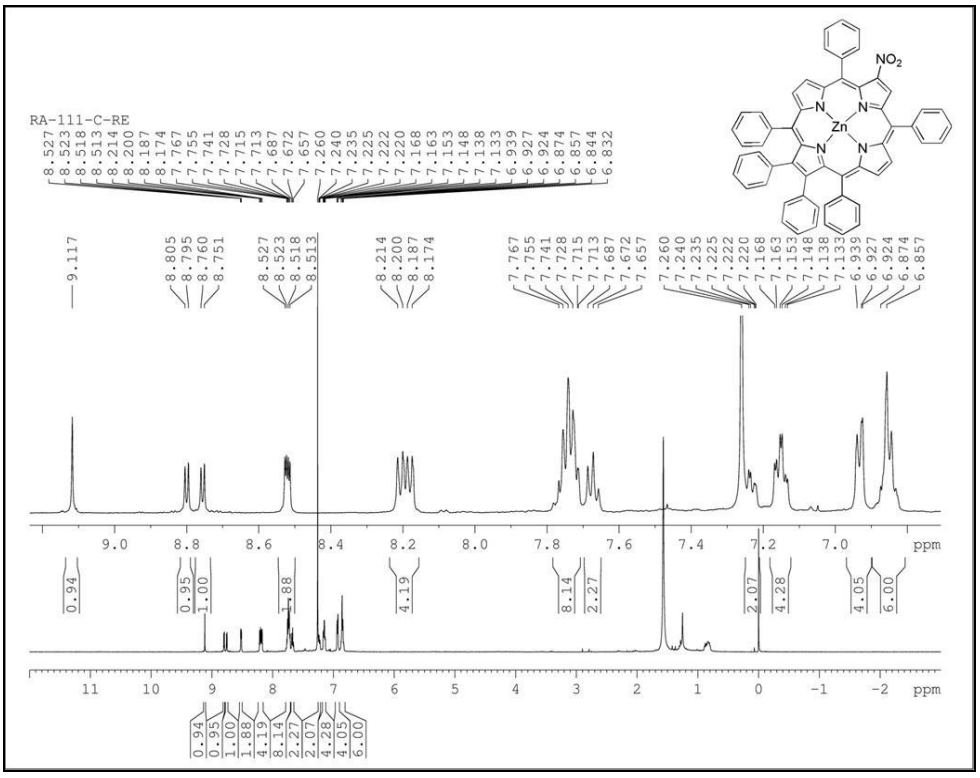


Figure S16. ^{1}H NMR spectrum of $H_2TPP(NO_2)(PE)_2$ in $CDCl_3$.

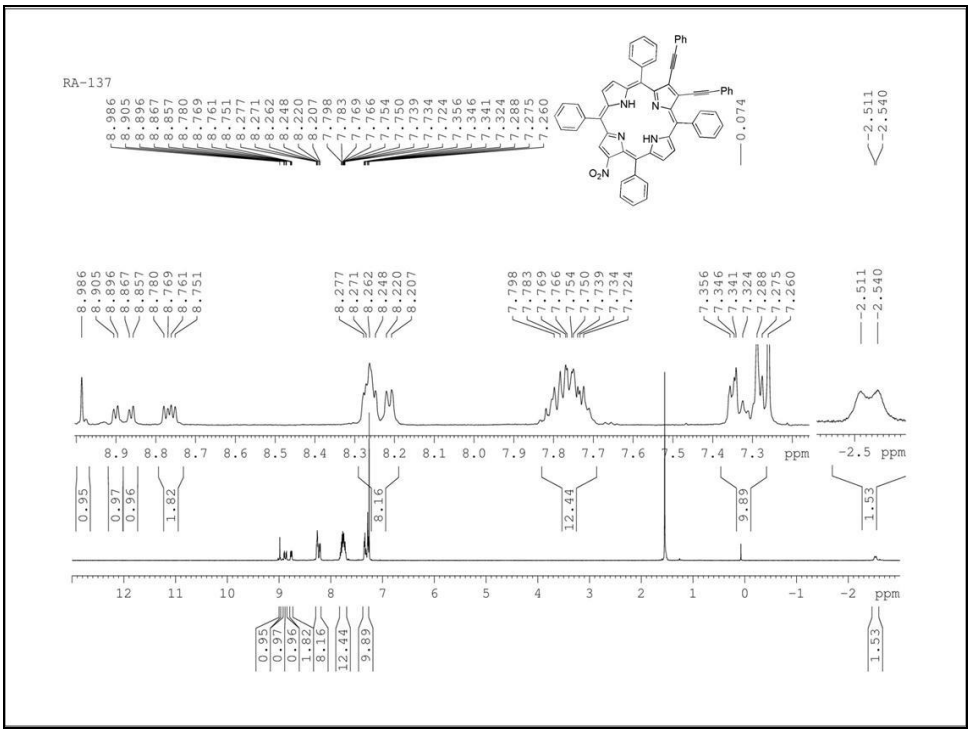


Figure S17.^{1}H NMR spectrum of $H_2TPP(NO_2)Th_2$ in $CDCl_3$**.**

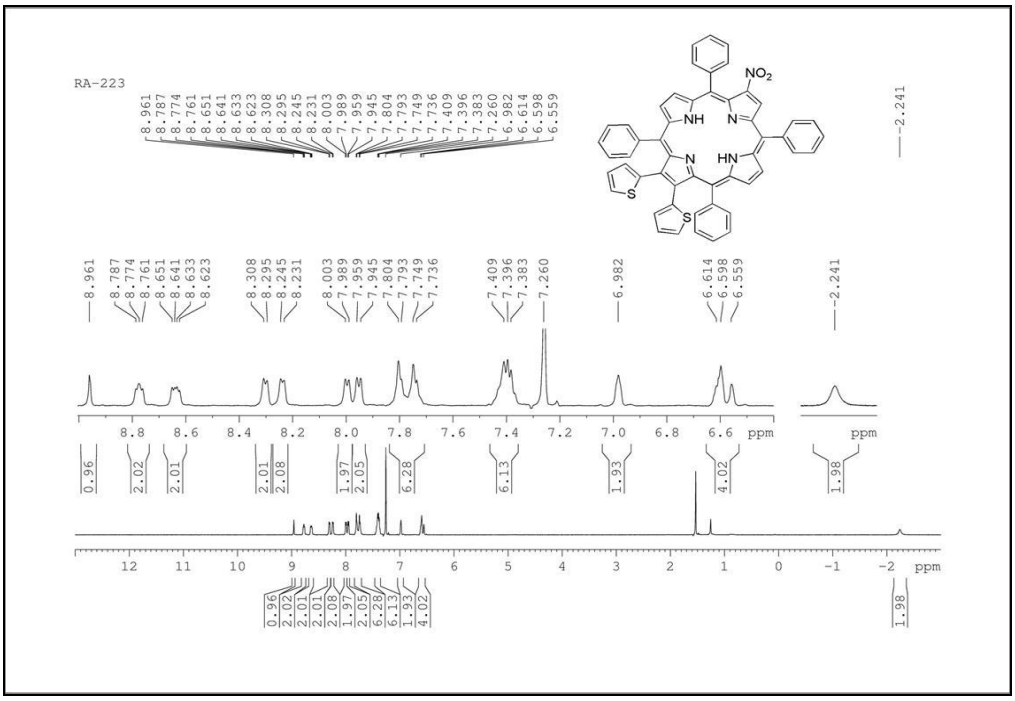


Figure S18. ^{1}H NMR spectrum of NiTPP(NO_2)Th_2 in $CDCl_3$.

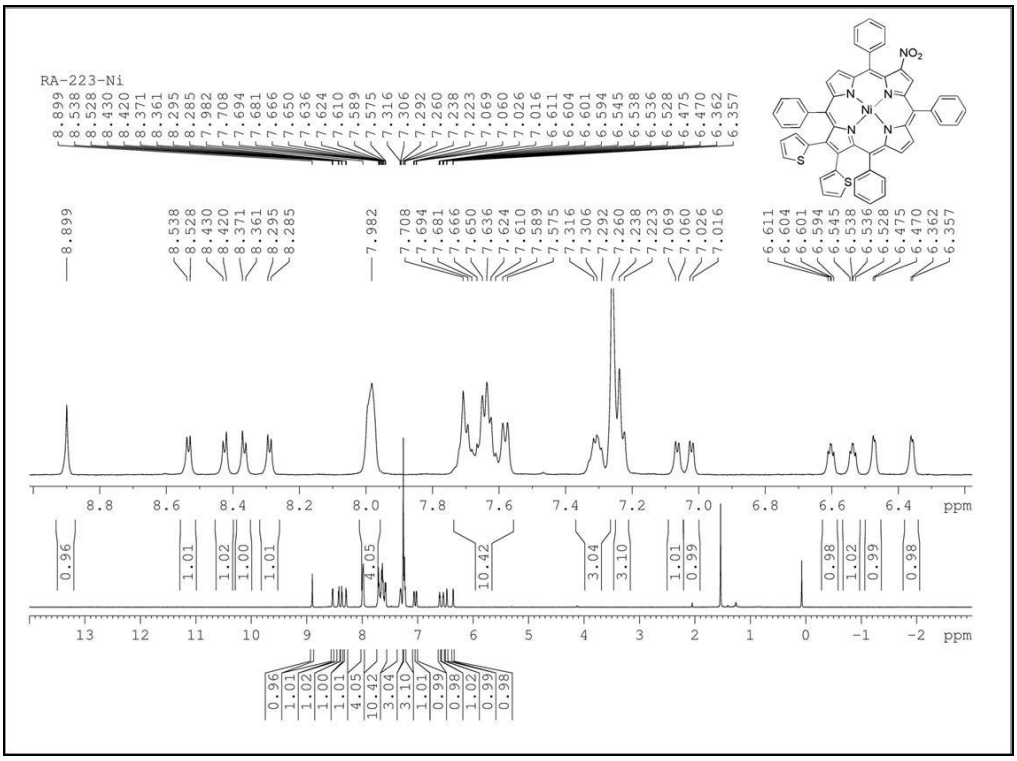


Figure S19.^{1}H NMR spectrum of ZnTPP(NO_2)Th_2 in $CDCl_3$**.**

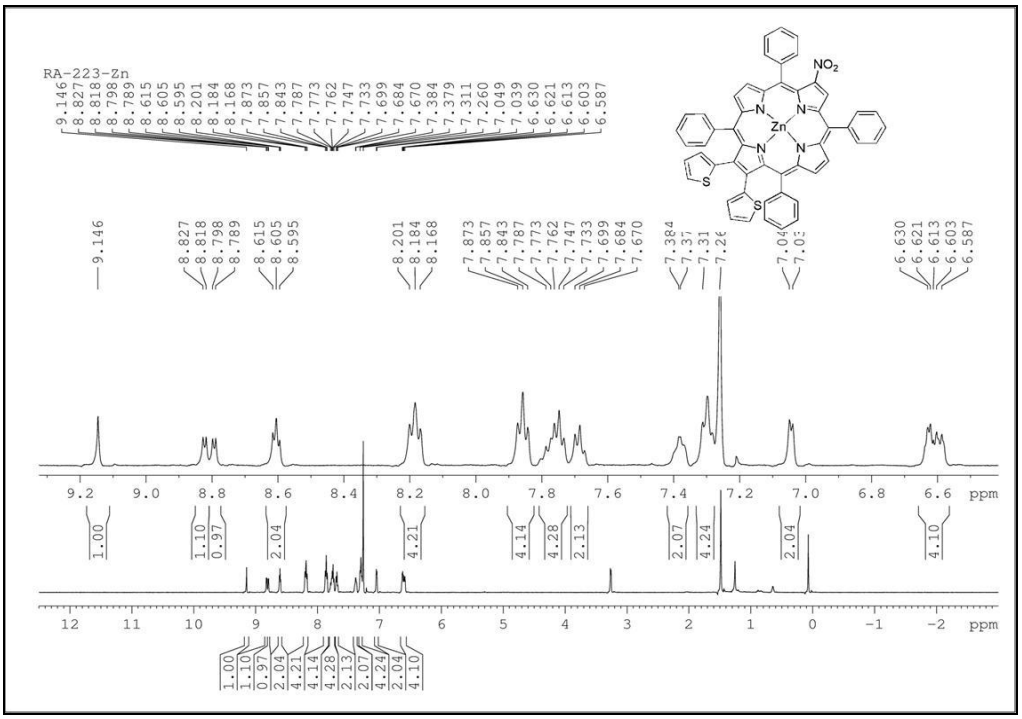


Figure S20. ^{1}H NMR spectrum of $H_2TPP(NO_2)(CN)_2$ in $CDCl_3$.

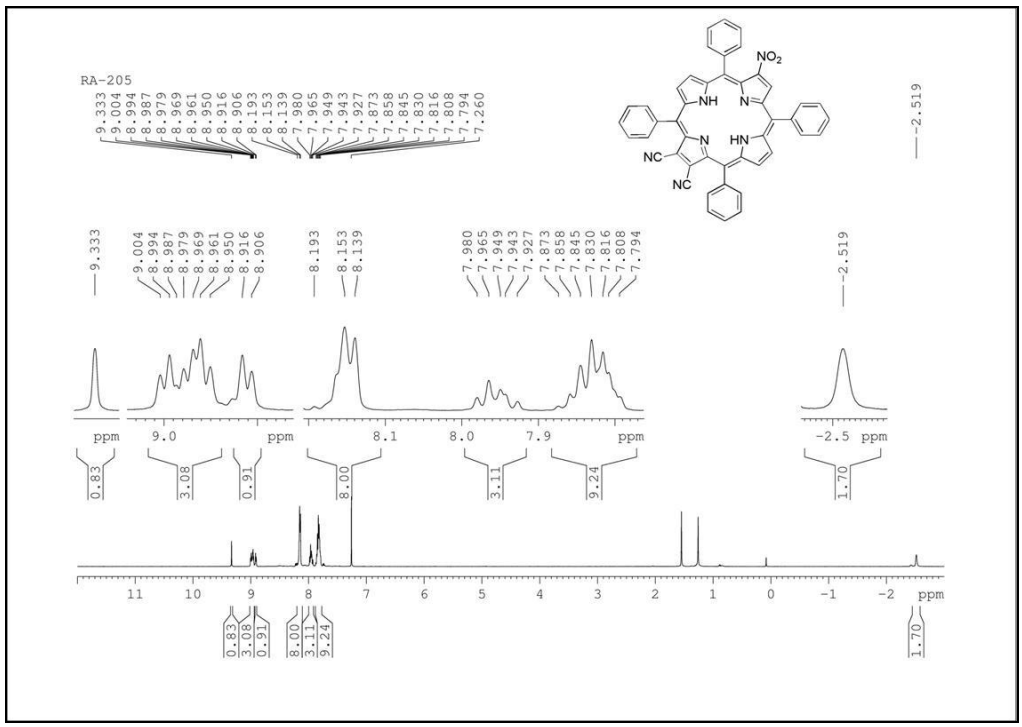


Figure S21. ^{1}H NMR spectrum of $NiTPP(NO_2)(CN)_2$ in $CDCl_3$.

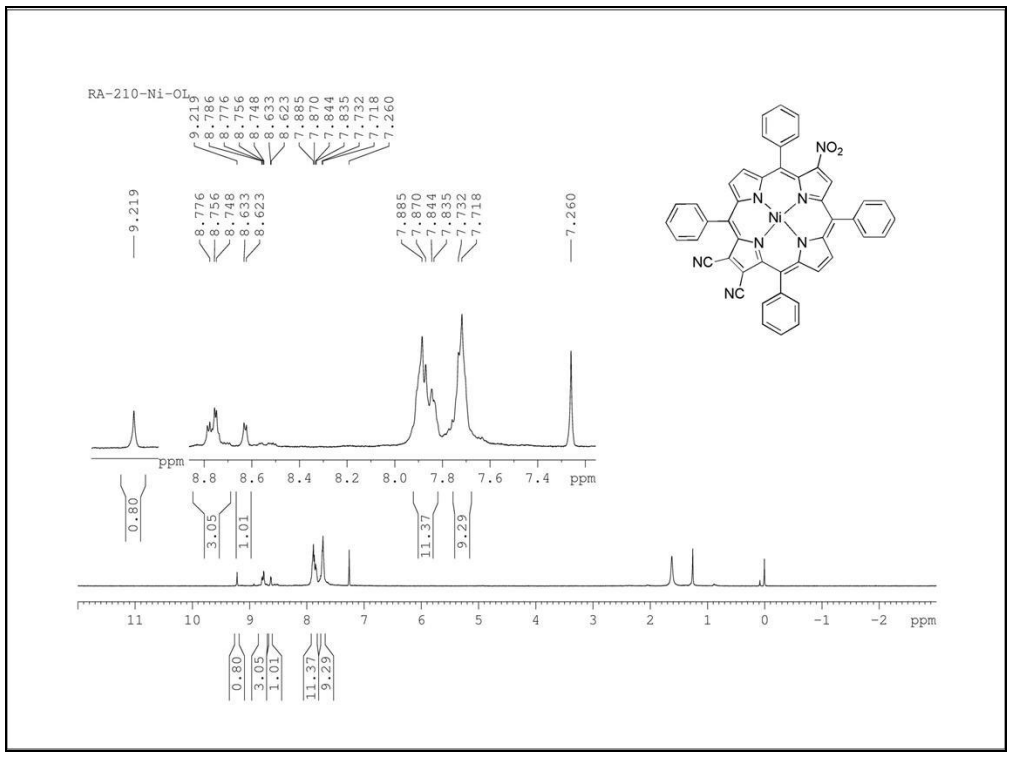


Figure S22. 1H NMR spectrum of $ZnTPP(NO_2)(CN)_2$ in $CDCl_3$.

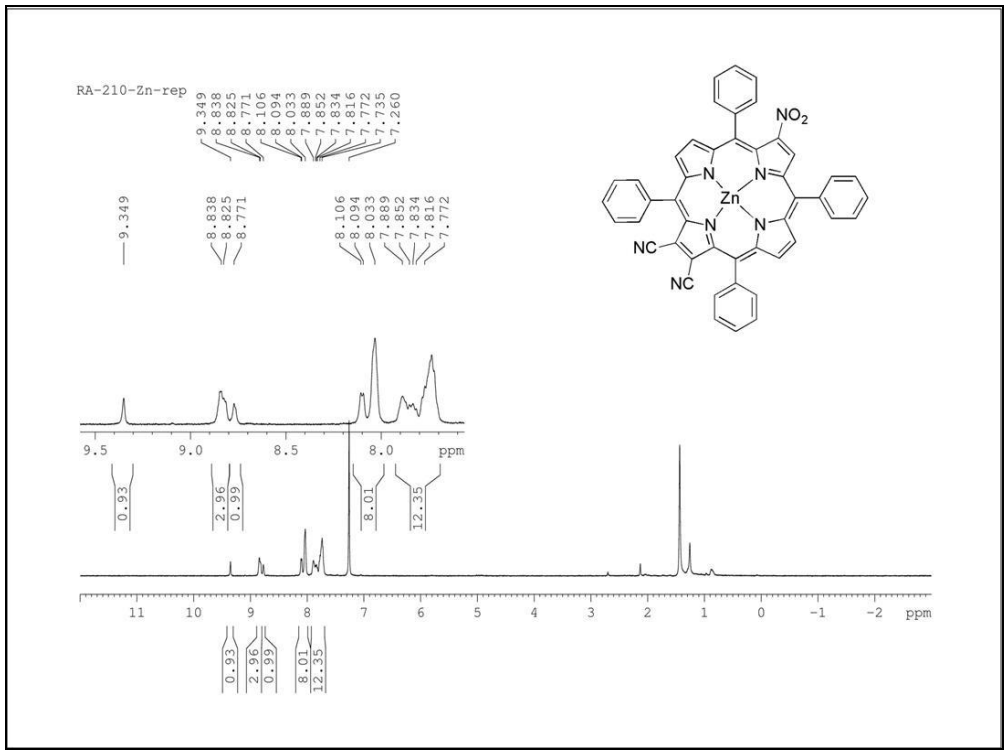


Figure S23. ^1H NMR spectrum of $NiTPP(NO_2)Br_6$ in $CDCl_3$.

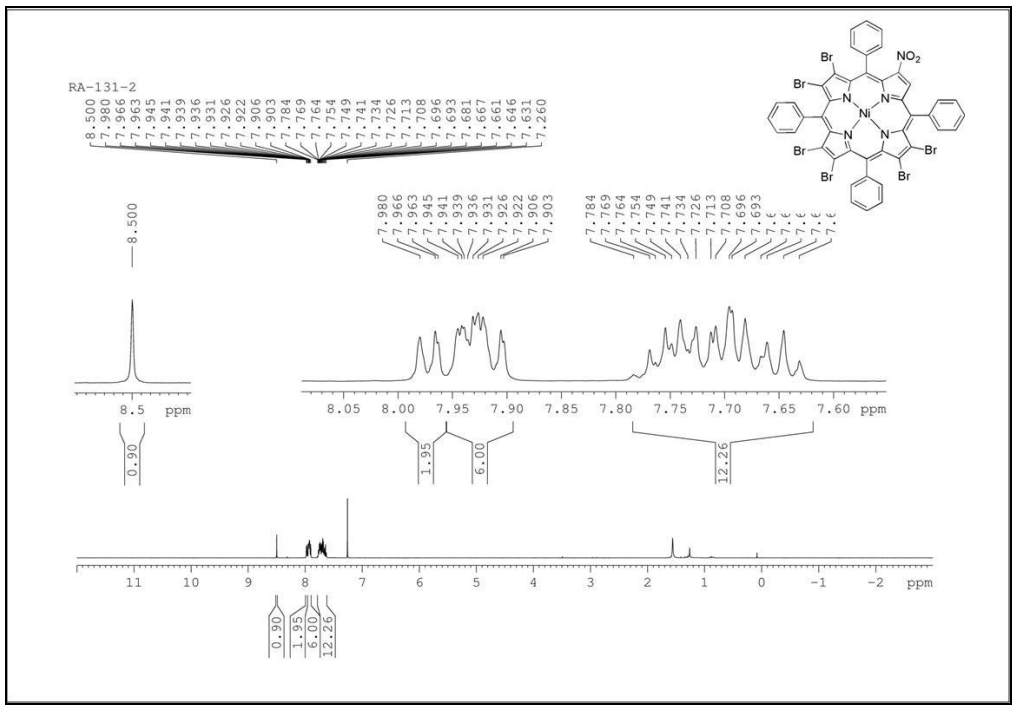


Figure S24. ^{1}H NMR spectrum of ZnTPP(NO_2)Br_6 in $CDCl_3$.

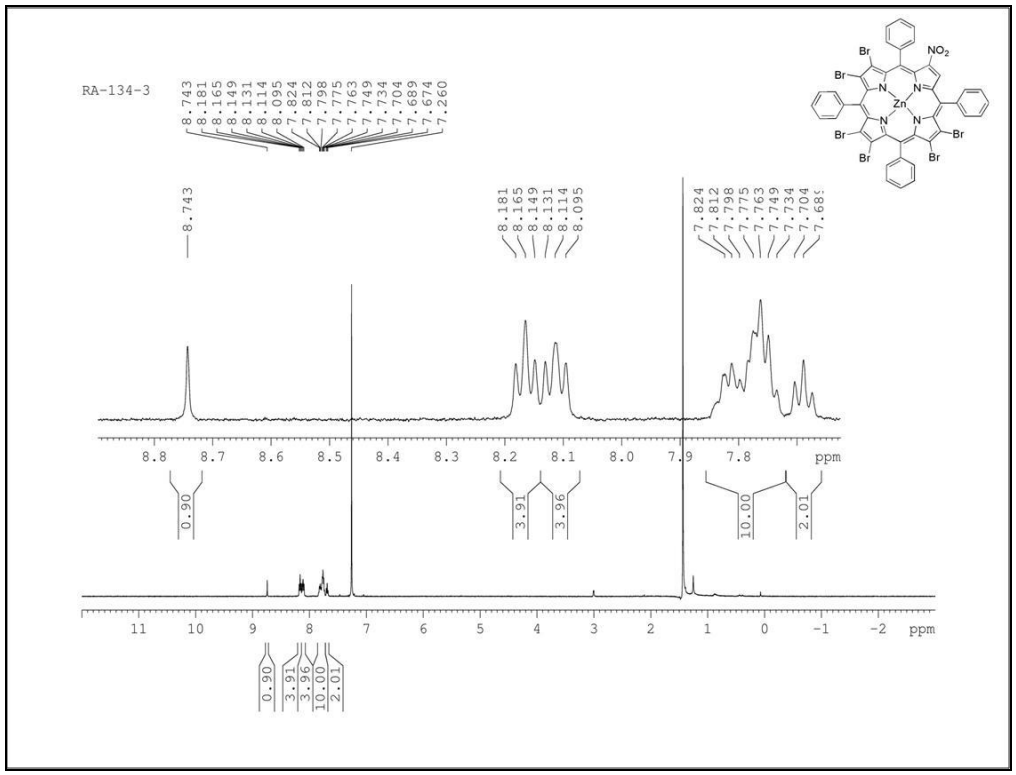


Figure S25. ^{1}H NMR spectrum of NiTPP(NO_2)Ph_6 in $CDCl_3$.

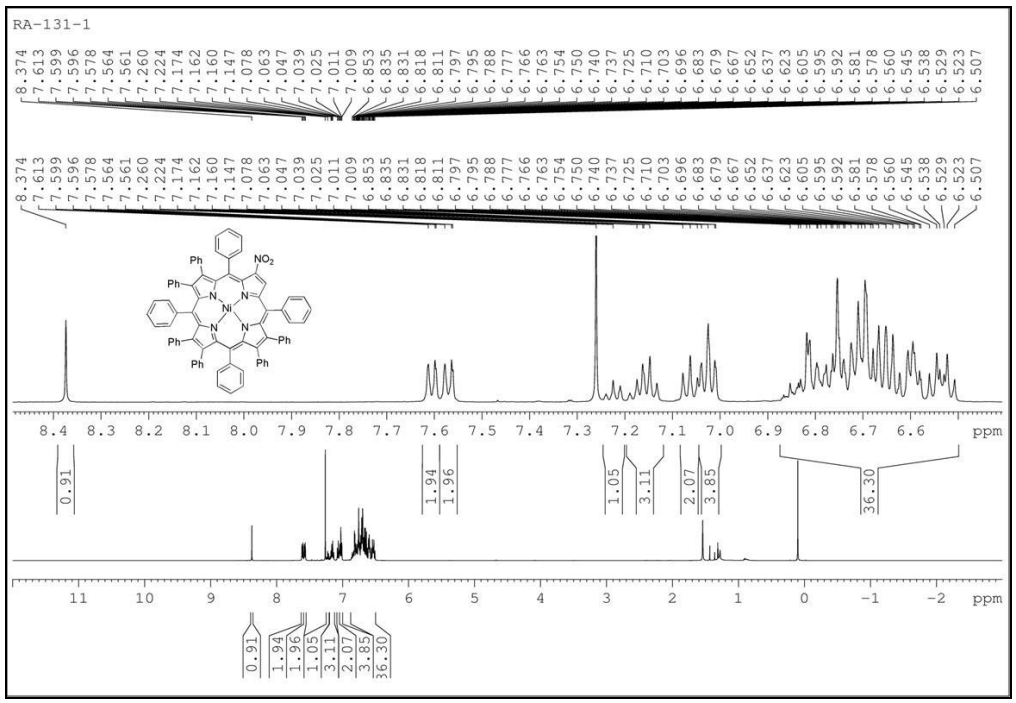


Figure S26. ^{1}H NMR spectrum of ZnTPP(NO_2)Ph_6 in $CDCl_3$.

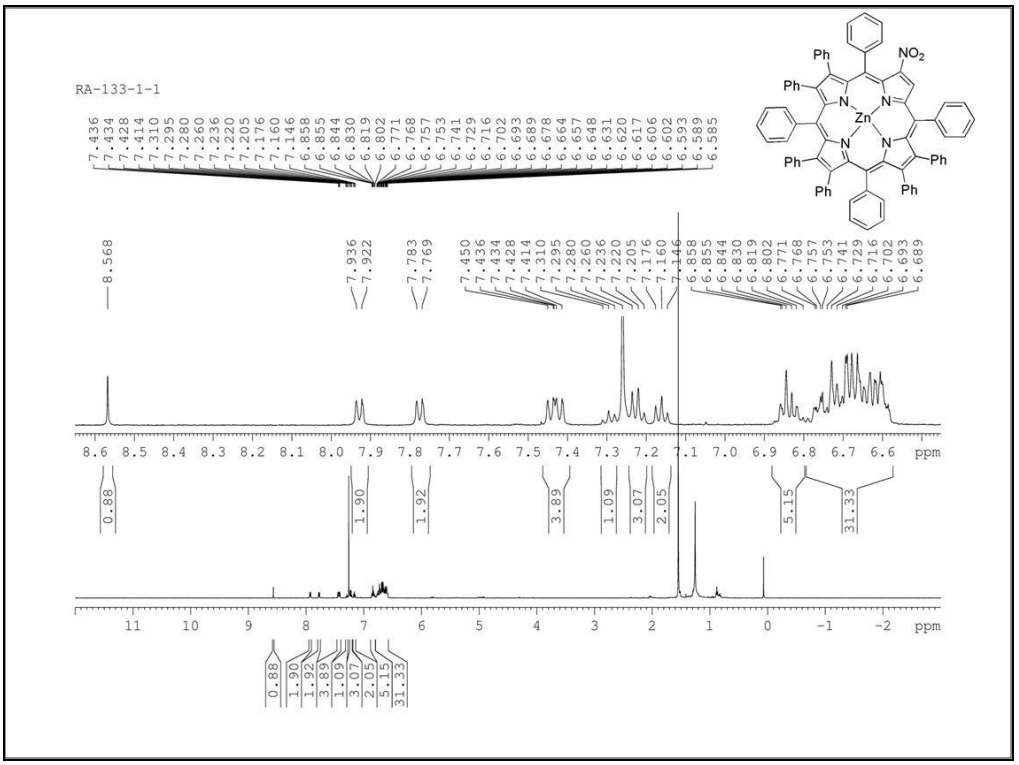


Figure S27. ^{1}H NMR spectrum of H_2TPP(NO_2)$(PE)_6$ in $CDCl_3$

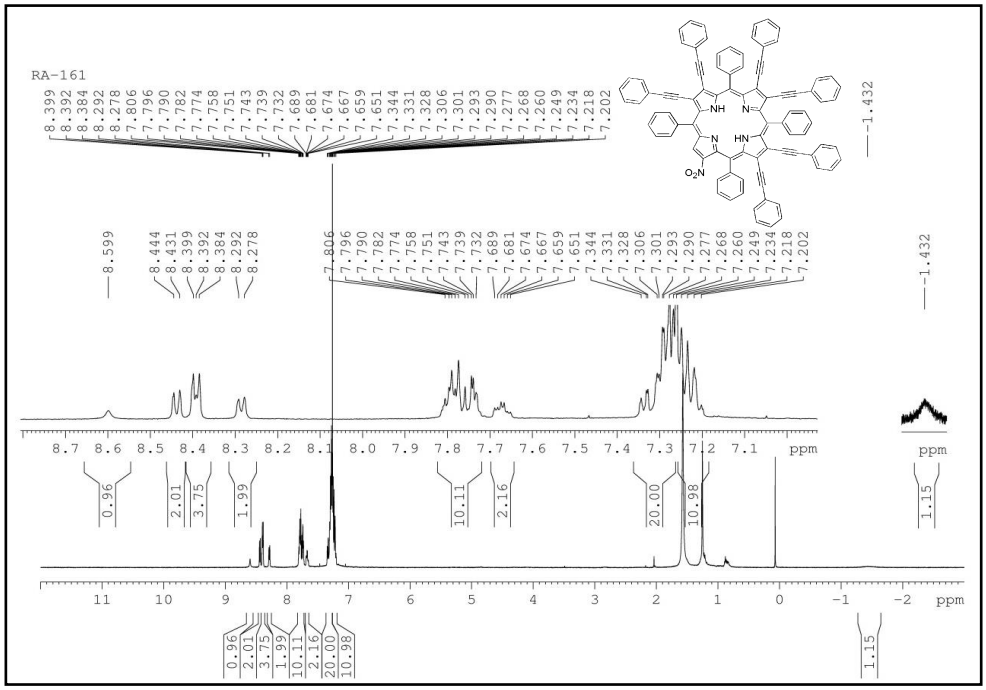


Figure S28. 1H NMR spectrum of NiTPP(NO_2)($PE)_6$ in $CDCl_3$

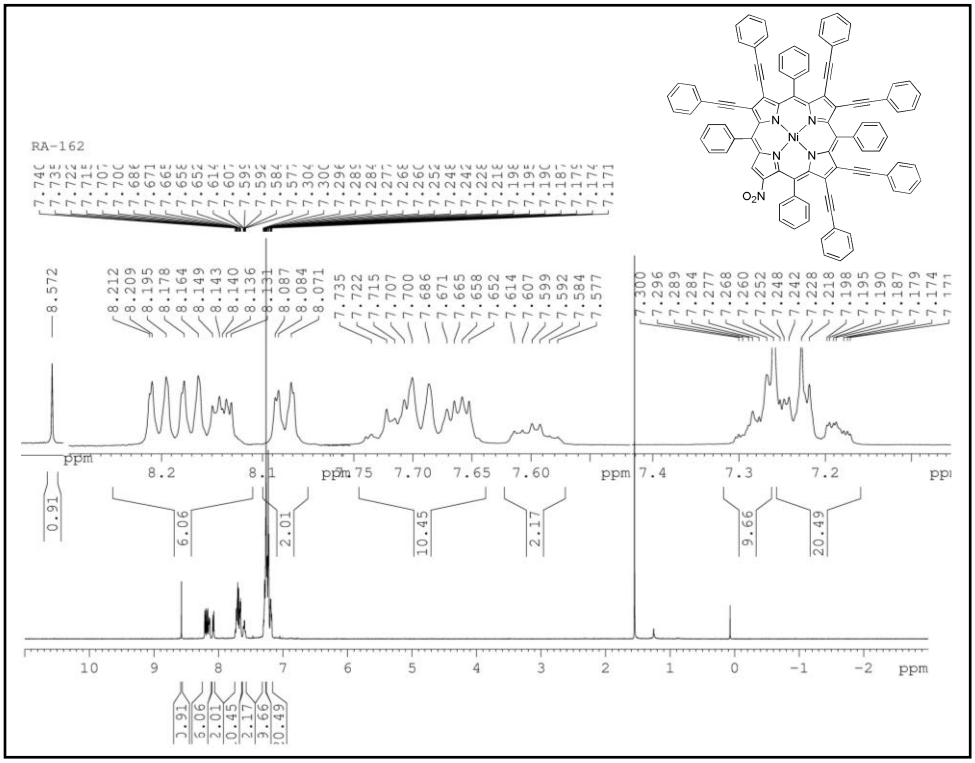


Figure S29. 1H NMR spectrum of ZnTPP(NO_2)($PE)_6$ in $CDCl_3$

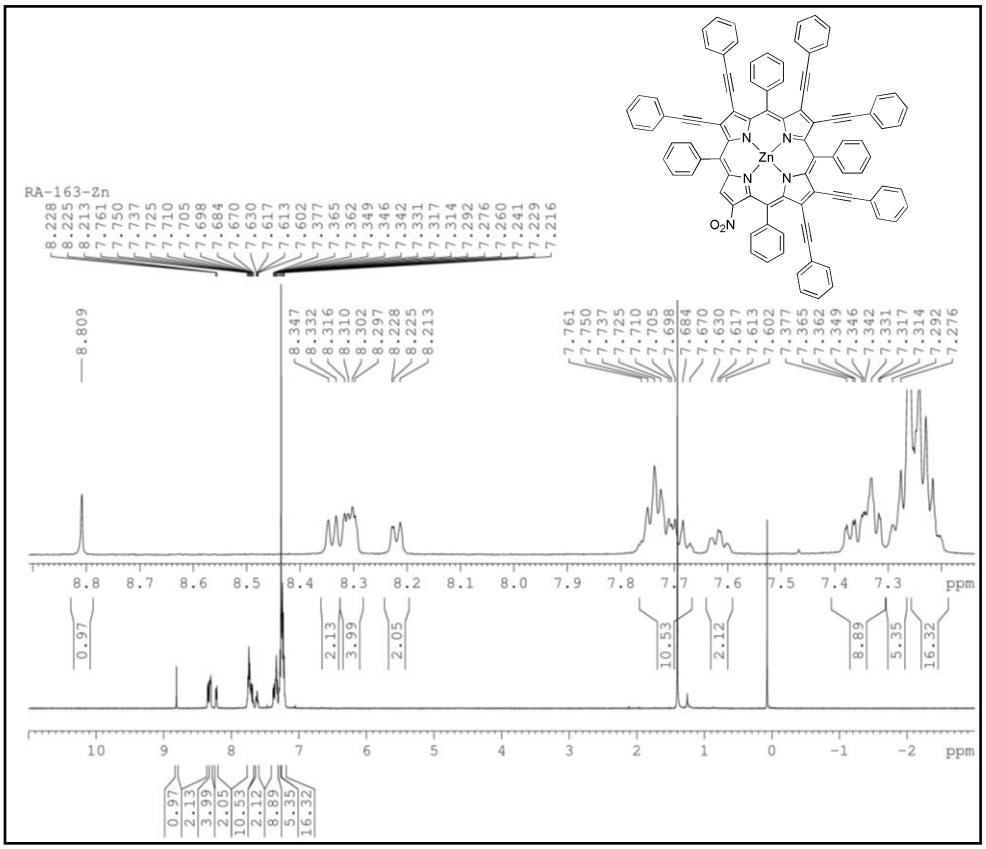
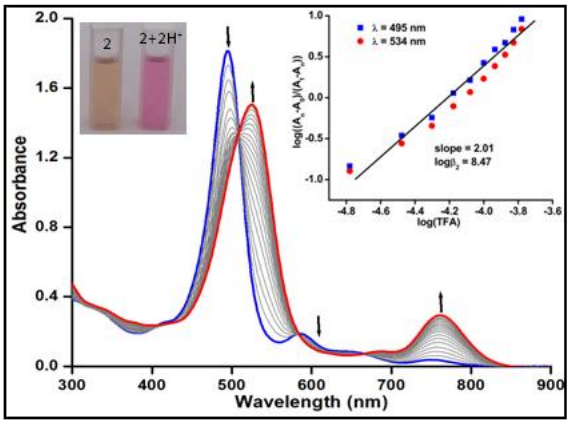
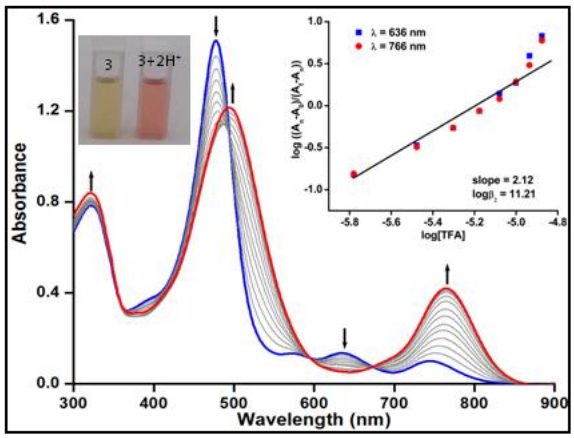


Figure S30. UV-Visible spectral changes during titration of **2-9** while increasing [TFA], insets show the corresponding Hill plots.

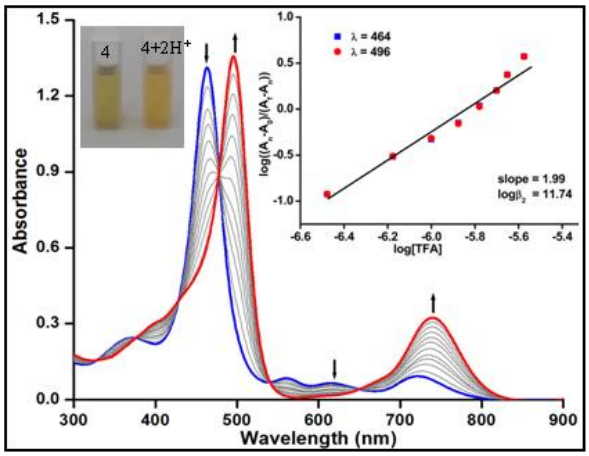
(a). $H_2TPP(NO_2)(PE)_6$ (2)



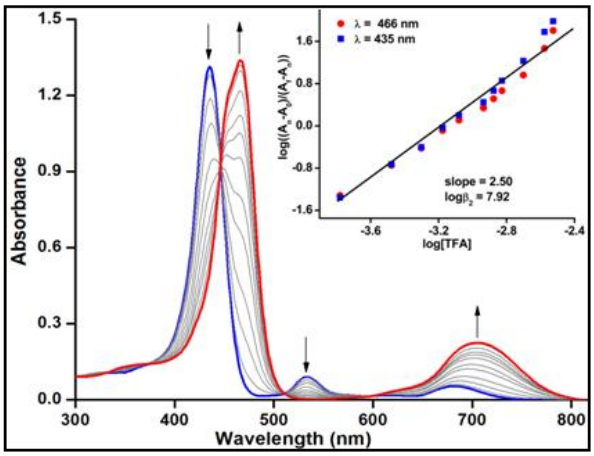
(b). $H_2TPP(NO_2)Th_6$ (3)



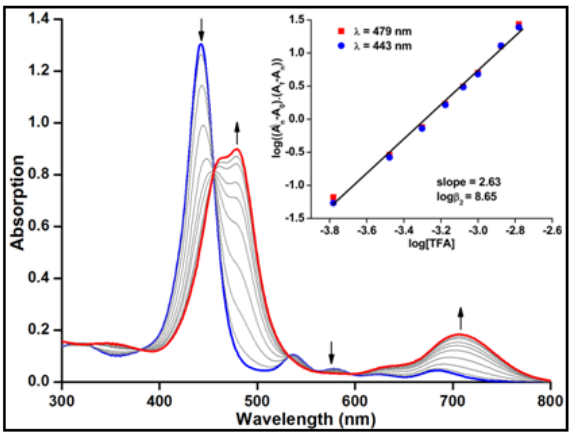
(c). $H_2TPP(NO_2)Ph_6$ (4)



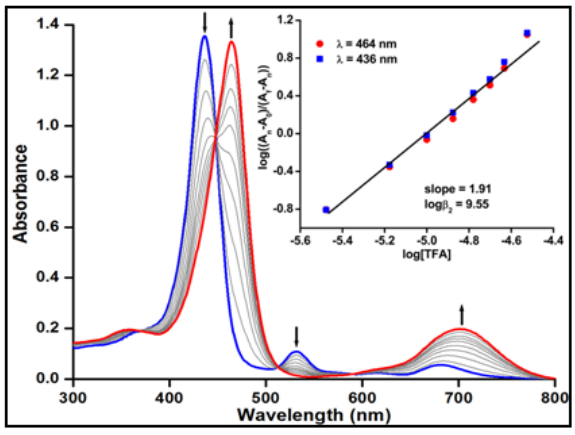
(d). $H_2TPP(NO_2)Br_2$ (5)



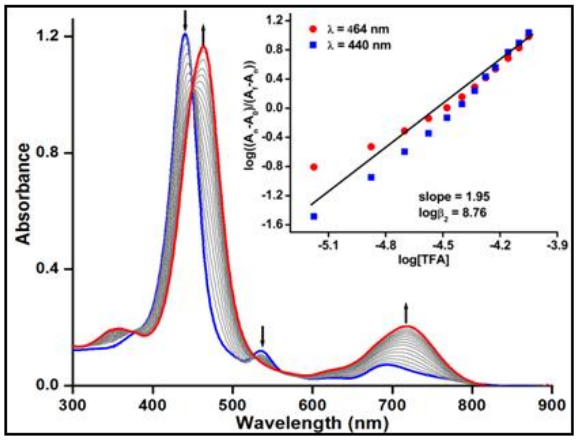
(e). $H_2TPP(NO_2)(PE)_2$ (6)



(f). $H_2TPP(NO_2)Ph_2$ (7)



(g). $H_2TPP(NO_2)Th_2$ (8)



(h). $H_2TPP(NO_2)CN_2$ (9)

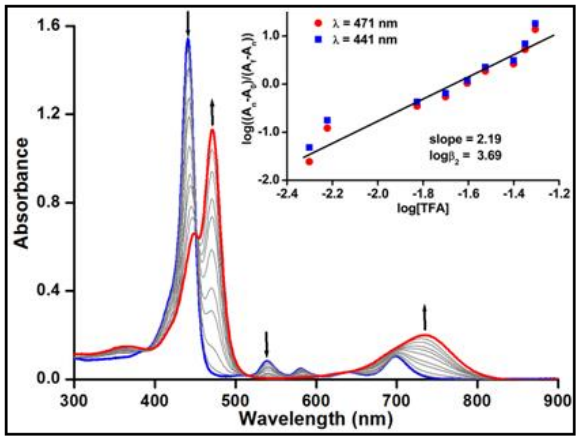
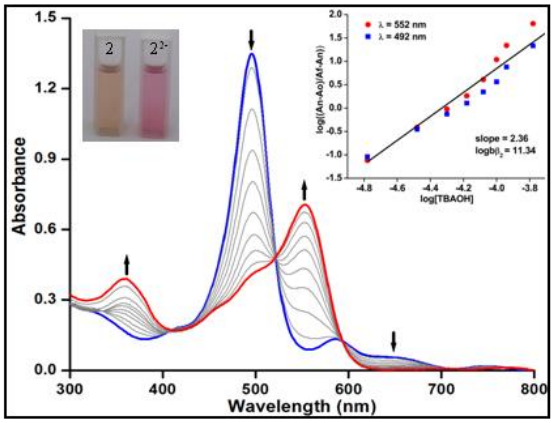
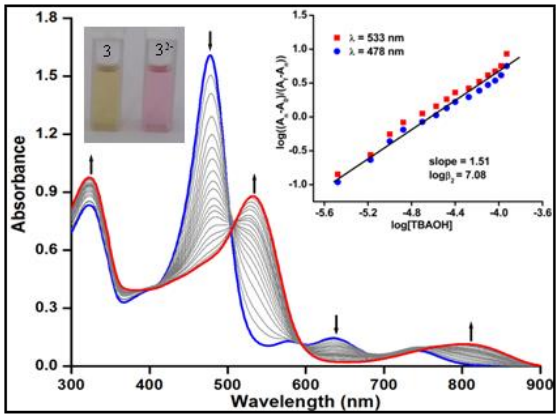


Figure S31. UV-Visible spectral changes during titration of TBAOH, insets show Hill plots.

(a). $H_2TPP(NO_2)(PE)_6$ (2)



(b). $H_2TPP(NO_2)Th_6$ (3)



(c). $H_2TPP(NO_2)Ph_6$ (4)

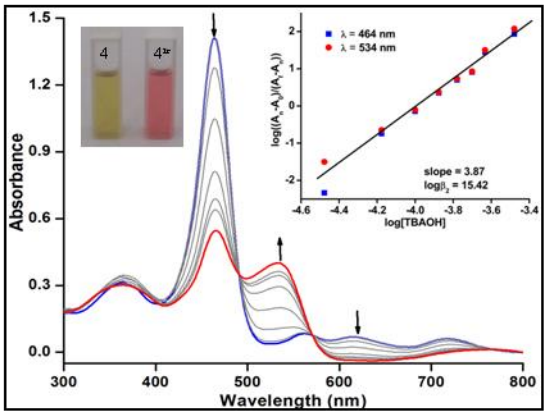


Table S7. Electrochemical redox data of various metal complexes of mixed substituted porphyrins in CH_2Cl_2 containing 0.1 M $TBAPF_6$ with a scan rate of 0.1 V/s at 298 K.

Porphyrin	Oxidation (mV)		Reduction (mV)			Metal Centred		ΔE (mV)
						Oxdn.	Redn.	
	I	II	I	II	III	I	II	
CoTPP	1060	1315	-1380			850	-860	2440
CoTPP(NO_2)	1175	1421	-1298			910	-661	2473
CoTPP(NO_2)Br_2	1223	1442	-1208			922	-515	2431
CoTPP(NO_2)Ph_2	1134	1348	-1292			886	-644	2426
CoTPP(NO_2)$(PE)_2$	1212	1414	-1187			957	-545	2399
CoTPP(NO_2)Th_2	1117	1317	-1260			881	-585	2377
CoTPP(NO_2)$(CN)_2$	1267	1391	-1147			965	-380	2414
CoTPP(NO_2)Br_6	1377	1513	-1103			1012	-269	2480
CoTPP(NO_2)Ph_6	1082	1192	-1382			801	-638	2463
CoTPP(NO_2)$(PE)_6$	1273	1397	-1073			1009	-337	2346
CoTPP(NO_2)Th_6	1158	-	-1253			884	-472	2411
NiTPP	1020	1315	-1280	-1720				2300
NiTPP(NO_2)	1187	1316	-948	-1212				2136
NiTPP(NO_2)Br_2	1242[a]	-	-829	-1061				2071
NiTPP(NO_2)Ph_2	1116	1241	-939	-1200				2055
NiTPP(NO_2)$(PE)_2$	1193	1306	-818	-1032				2011
NiTPP(NO_2)Th_2	1119	1238	-908	-1137				2027
NiTPP(NO_2)$(CN)_2$	1296[a]	-	-734	-966				2030
NiTPP(NO_2)Br_6	1305[a]	-	-703	-950				2008
NiTPP(NO_2)Ph_6	956	1183	-988	-1275				1944
NiTPP(NO_2)$(PE)_6$	1244[a]	-	-732	-943				1976
NiTPP(NO_2)Th_6	1018	1266	-902	-1165				1920
CuTPP	970	1350	-1325	-1705				2295
CuTPP(NO_2)	1076	1442	-979	-1229				2055
CuTPP(NO_2)Br_2	1072	1491	-856	-1074				1928
CuTPP(NO_2)Ph_2	962	1320	-967	-1214				1929
CuTPP(NO_2)$(PE)_2$	1061	1456	-847	-1055				1908

$CuTPP(NO_2)Th_2$	956	1402	-911	-1140		1867
$CuTPP(NO_2)(CN)_2$	1331	1599	-626	-1049		1957
$CuTPP(NO_2)Br_6$	1066	1609	-693	-922		1753
$CuTPP(NO_2)Ph_6$	698	1213	-985	-1288		1683
$CuTPP(NO_2)(PE)_6$	1013	1498	-749	-944	-1421	1762
$CuTPP(NO_2)Th_6$	780	1305	-864	-1163		1644
ZnTPP	835	1140	-1360	-1765		2195
$ZnTPP(NO_2)$	913	1217	-1048[i]	-1192	-1500	1961
$ZnTPP(NO_2)Br_2$	948	1182	-939[i]	-1080		1887
$ZnTPP(NO_2)Ph_2$	850	1074	-1064[i]	-1204	-1498	1914
$ZnTPP(NO_2)(PE)_2$	933	1181	-953[i]	-1085		1886
$ZnTPP(NO_2)Th_2$	875	1106	-993[i]	-1126	-1376	1868
$ZnTPP(NO_2)(CN)_2$	1069	1429	-698	-1089		1767
$ZnTPP(NO_2)Br_6$	931	1192	-839[i]	-977	-1227	1770
$ZnTPP(NO_2)Ph_6$	686	853	-1076[i]	-1377[i]		1762
$ZnTPP(NO_2)(PE)_6$	925	1176	-858[i]	-976		1783
$ZnTPP(NO_2)Th_6$	754	985	-931[i]	-1106	-1496	1685

[a]refers two electron oxidation and [i]refers to irreversible

Figure S32. UV-Visible spectral changes of Co(II) porphyrins upon addition of *tert*-butyl hydroperoxide (conversion of Co(II) to Co(III) porphyrins) in CH_2Cl_2 at 298 K.

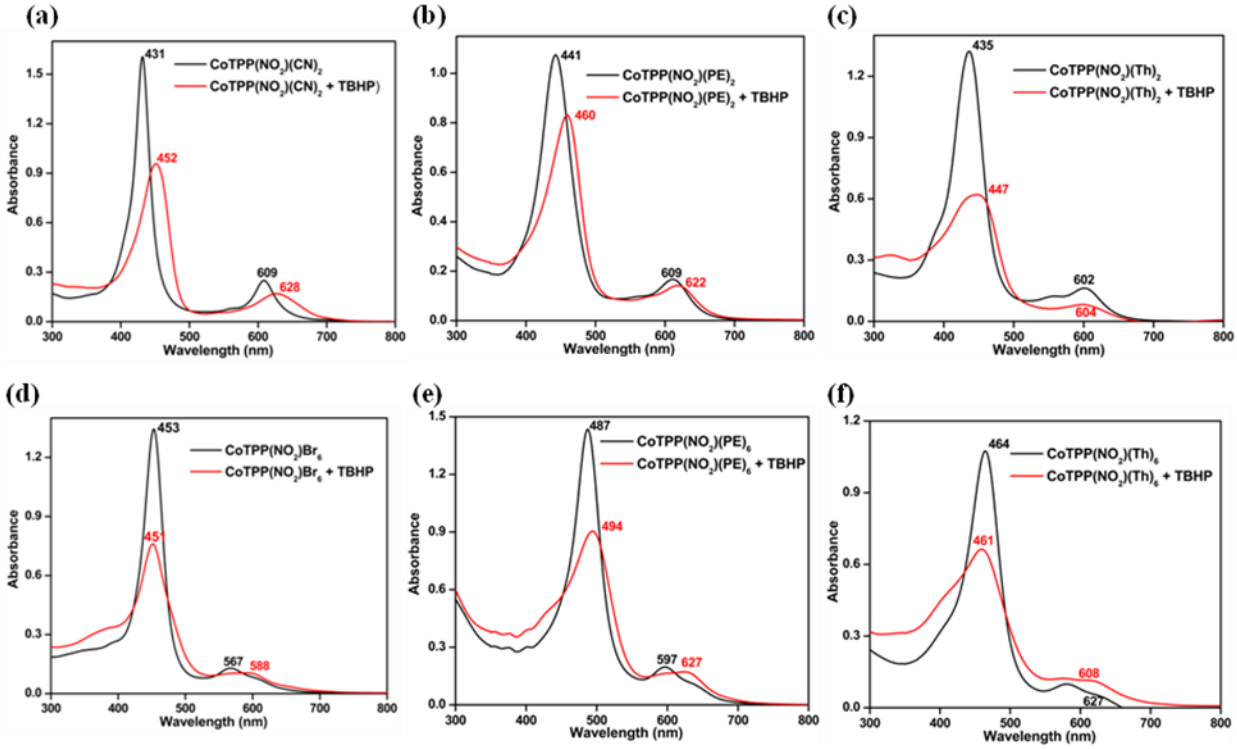
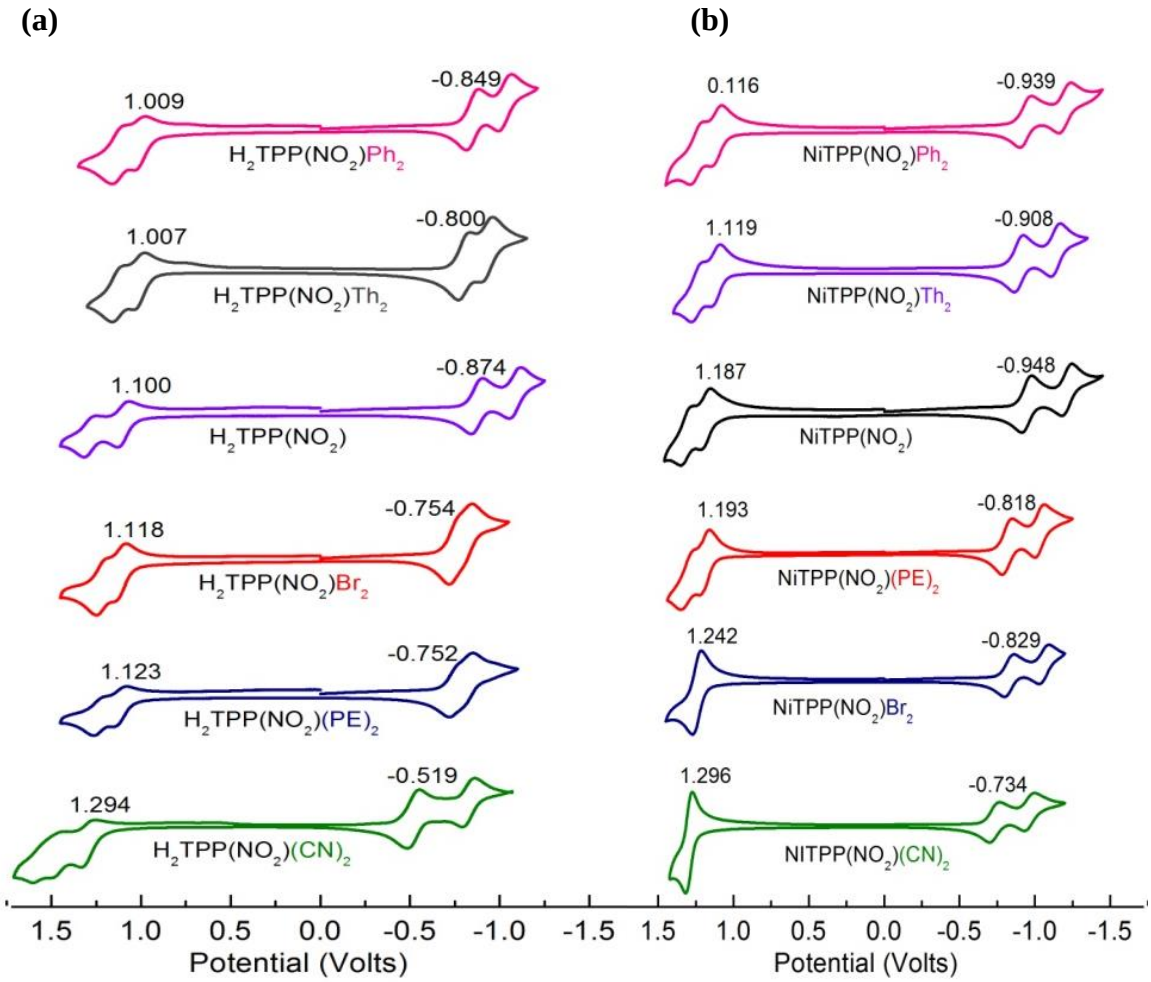
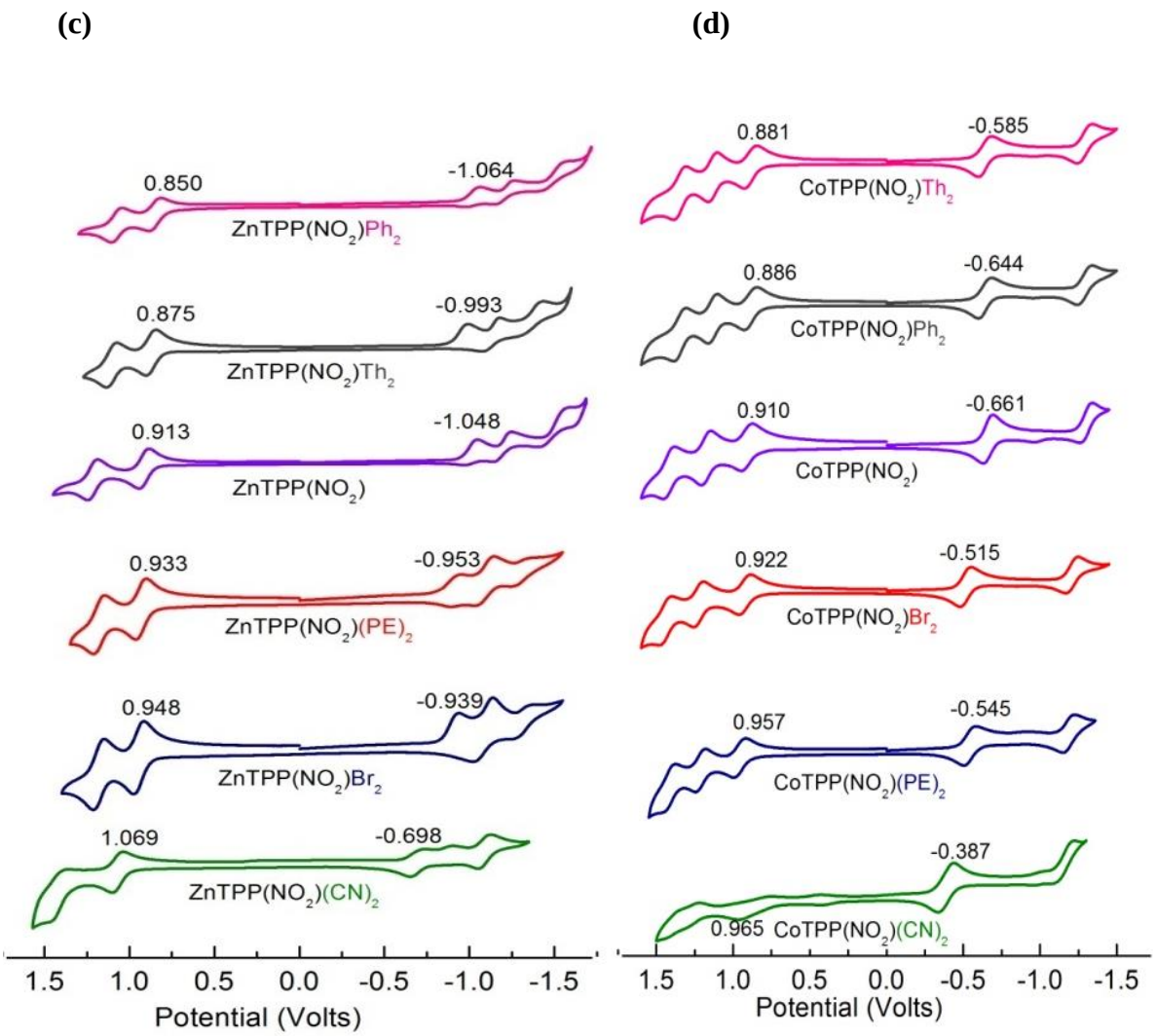


Table S8. UV-Visible spectral data of Co(II) and Co(III) porphyrins in CH_2Cl_2 at 298 K.

Porphyrin	**Without TBHP (Co^{II})**		**With TBHP (Co^{III})**	
	B band, nm	Q band(s), nm	B band, nm	Q band(s), nm
$CoTPP(NO_2)$	420	540, 578	442	557
$CoTPP(NO_2)Br_2$	431	551, 595	450	597
$CoTPP(NO_2)Ph_2$	434	553, 593	430	588
$CoTPP(NO_2)(PE)_2$	441	609	460	620
$CoTPP(NO_2)Th_2$	435	602	447	604
$CoTPP(NO_2)(CN)_2$	431	609	452	628
$CoTPP(NO_2)Br_6$	453	567	451	588
$CoTPP(NO_2)Ph_6$	454	570, 611	446	604
$CoTPP(NO_2)(PE)_6$	487	597	494	627
$CoTPP(NO_2)Th_6$	464	580, 627	461	608

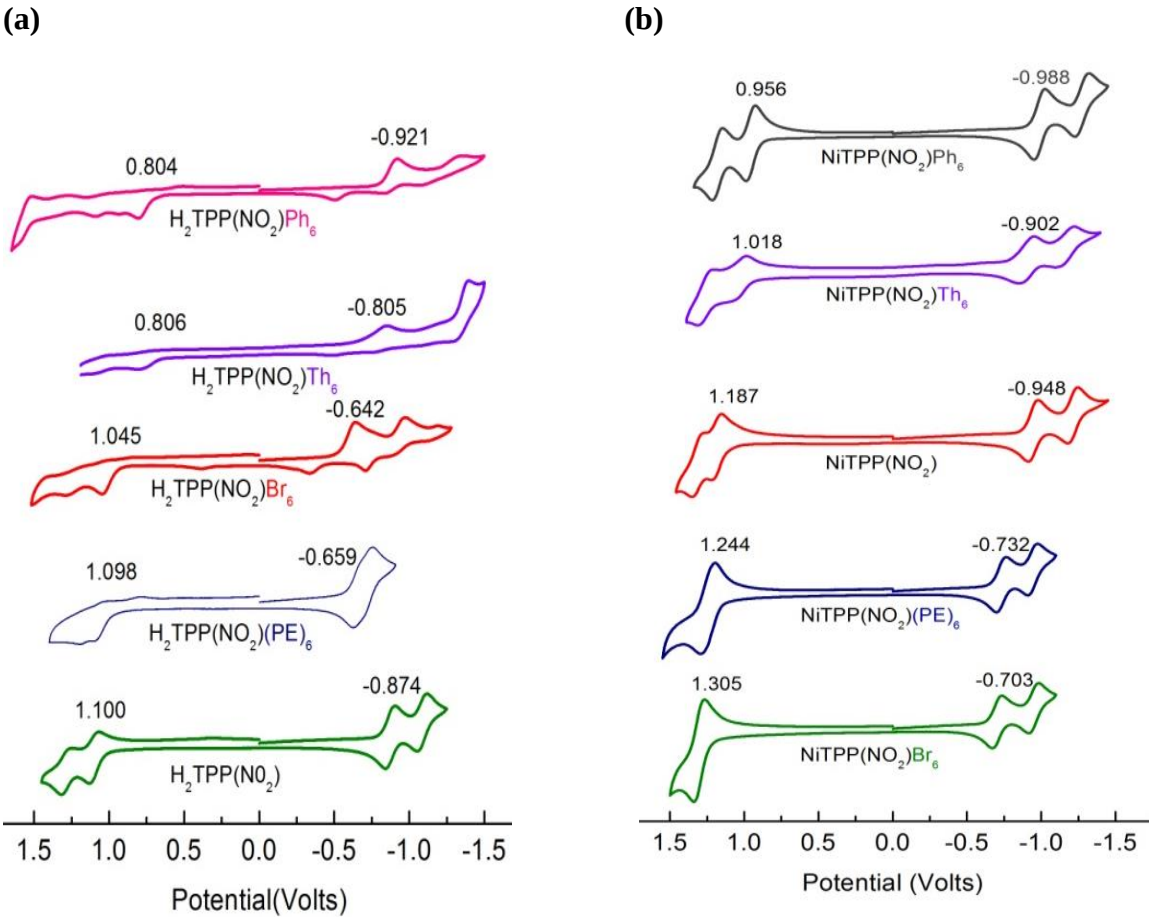
Figure S33. Cyclic voltammograms of (a) $H_2TPP(NO_2)X_2$, (b) $NiTPP(NO_2)X_2$, (c) $ZnTPP(NO_2)X_2$, (d) $CoTPP(NO_2)X_2$ (where X = H, Br, CN, PE, Th and Ph) complexes in CH_2Cl_2[a].



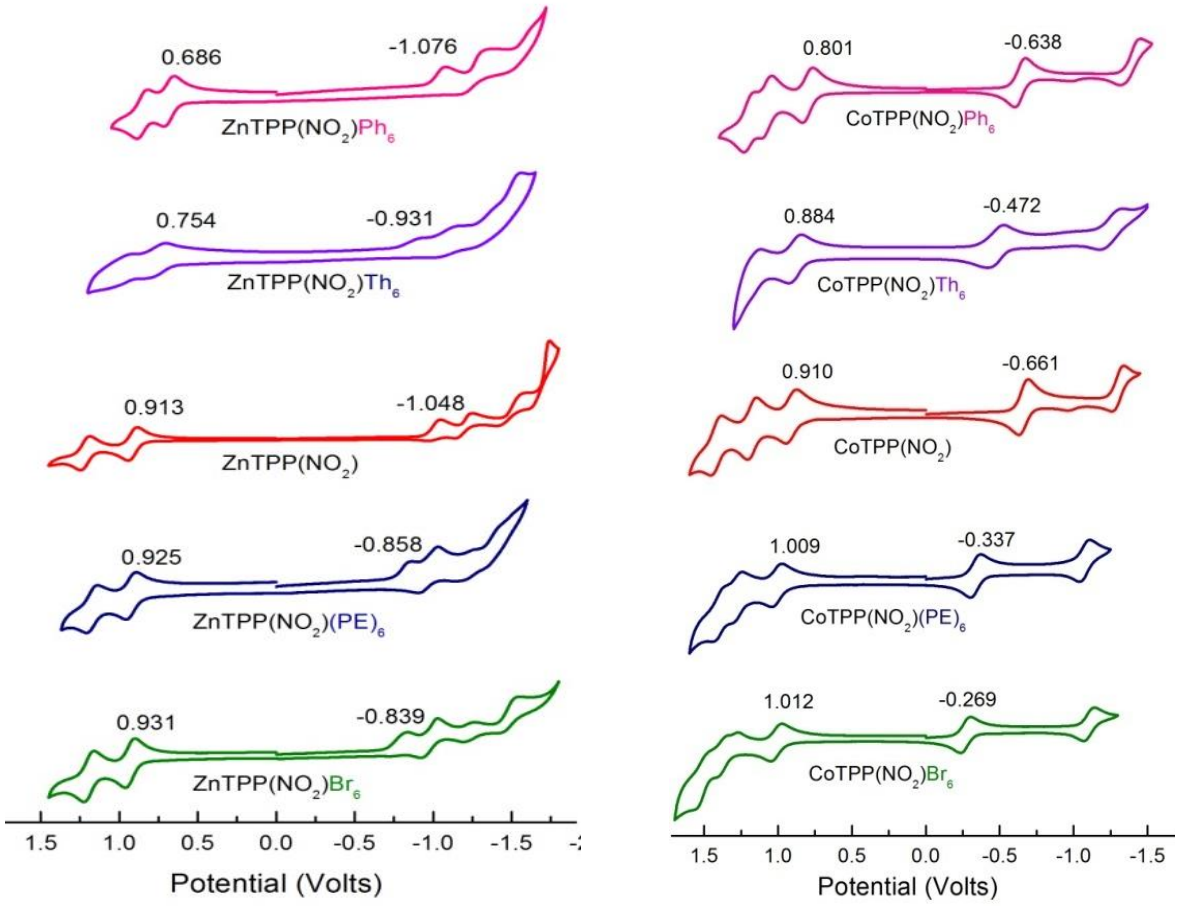


[a]Containing 0.1M $TBAPF_6$ with a scan rate of 0.1 V/s. Pt Working electrode, Ag/AgCl Reference electrode and Pt wire counter electrode were used.

Figure S34. Cyclic voltammograms of (a) $H_2TPP(NO_2)X_6$, (b) $NiTPP(NO_2)X_6$, (c) $ZnTPP(NO_2)X_6$, (d) $CoTPP(NO_2)X_6$ (where X = H, Br, PE, Th and Ph) complexes in CH_2Cl_2.

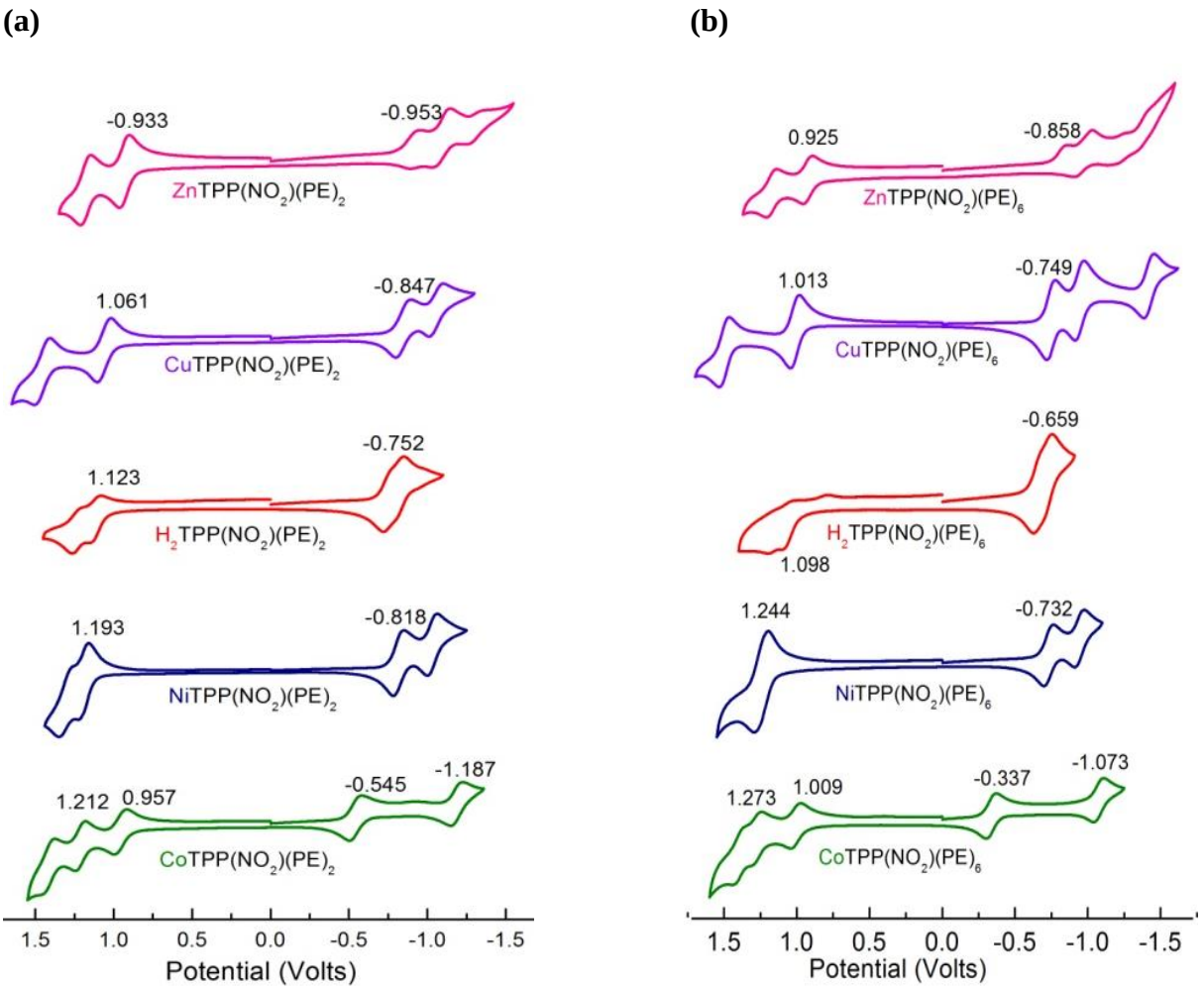


(c) **(d)**



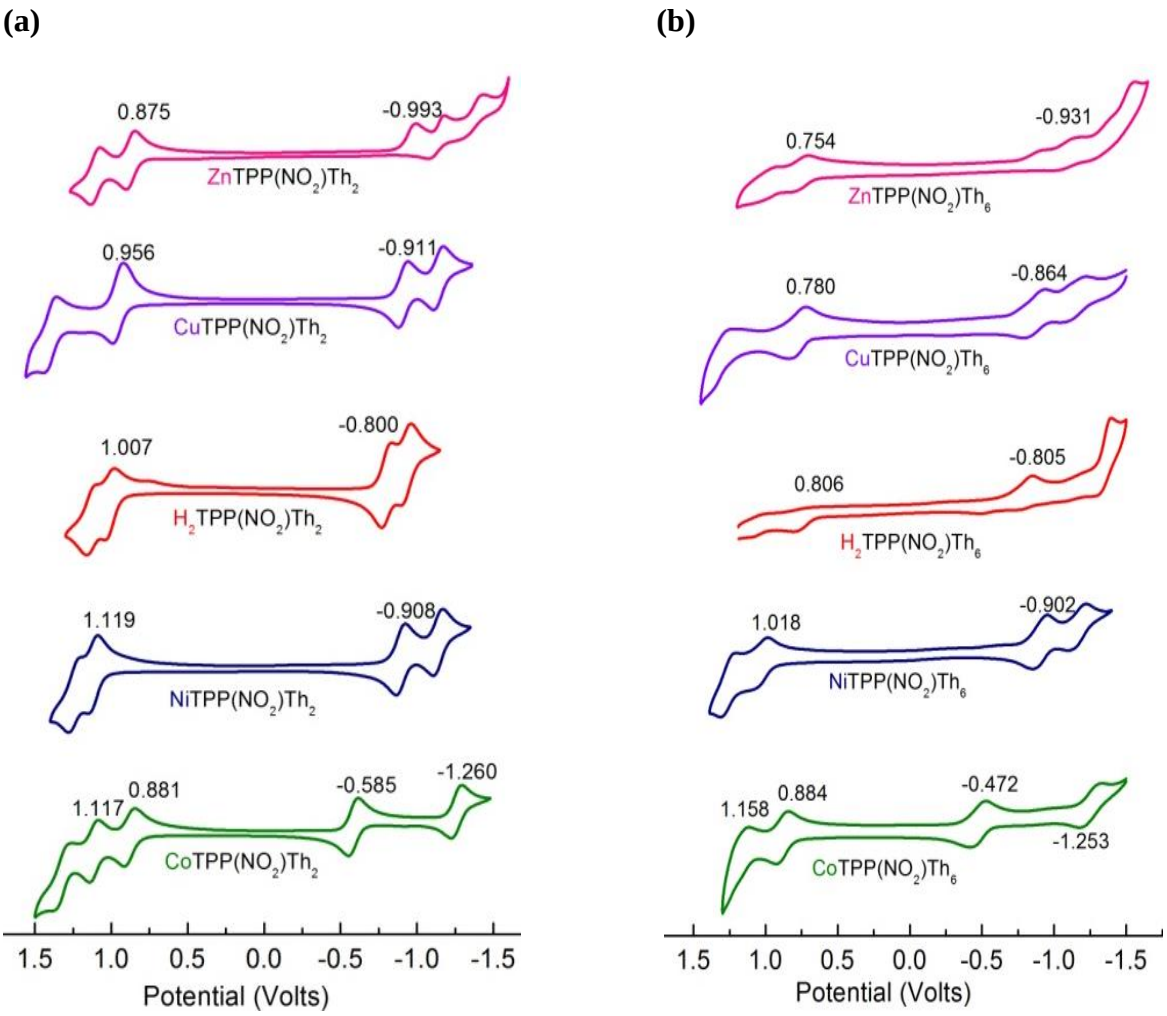
[a]Containing 0.1M TBAPF6 with a scan rate of 0.1 V/s. Pt Working electrode, Ag/AgCl Reference electrode and Pt wire counter electrode were used.

Figure S35. Cyclic voltammograms of (a) $MTPP(NO_2)(PE)_2$, (b) $MTPP(NO_2)(PE)_6$ where M = 2H, Cu(II), Zn(II), Ni(II), and Co(II) in CH_2Cl_2[a].



[a]Containing 0.1M TBAPF6 with a scan rate of 0.1 V/s. Pt Working electrode, Ag/AgCl Reference electrode and Pt wire counter electrode were used.

Figure S36. Cyclic voltammograms of (a) $MTPP(NO_2)Th_2$, (b) $MTPP(NO_2)Th_6$ where M = 2H, Cu(II), Zn(II), Ni(II), and Co(II) in CH_2Cl_2[a].



[a]Containing 0.1M TBAPF6 with a scan rate of 0.1 V/s. Pt Working electrode, Ag/AgCl Reference electrode and Pt wire counter electrode were used.

Figure S37. The HOMO-LUMO variation of CuTPP(NO_2)X_2 where X = PE, Br, Ph and Th in comparison to CuTPP(NO_2) and CuTPP.

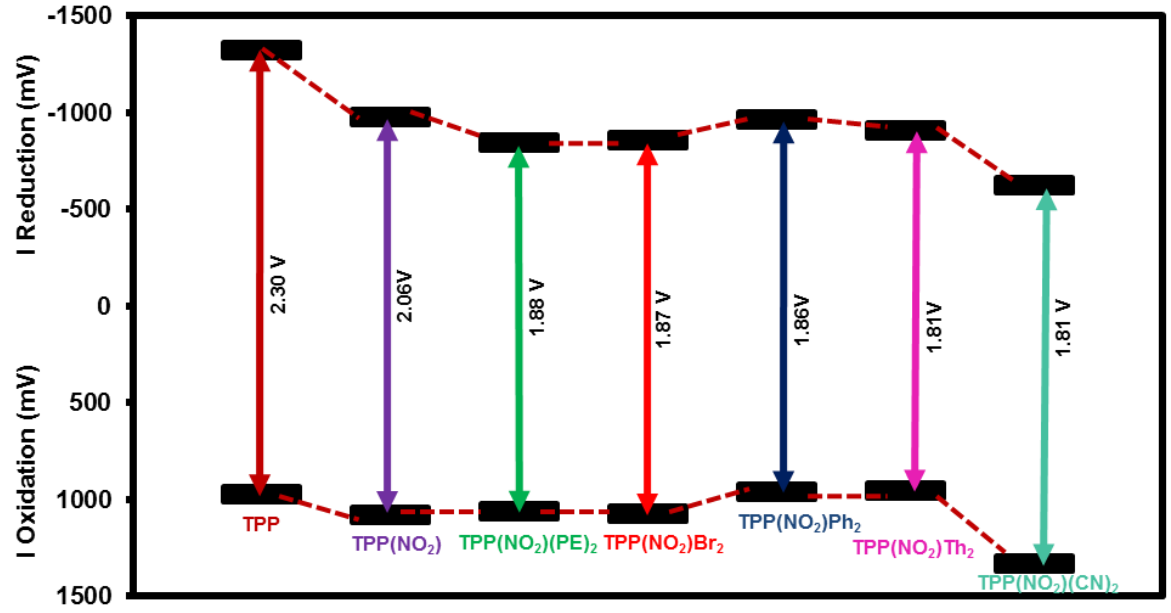
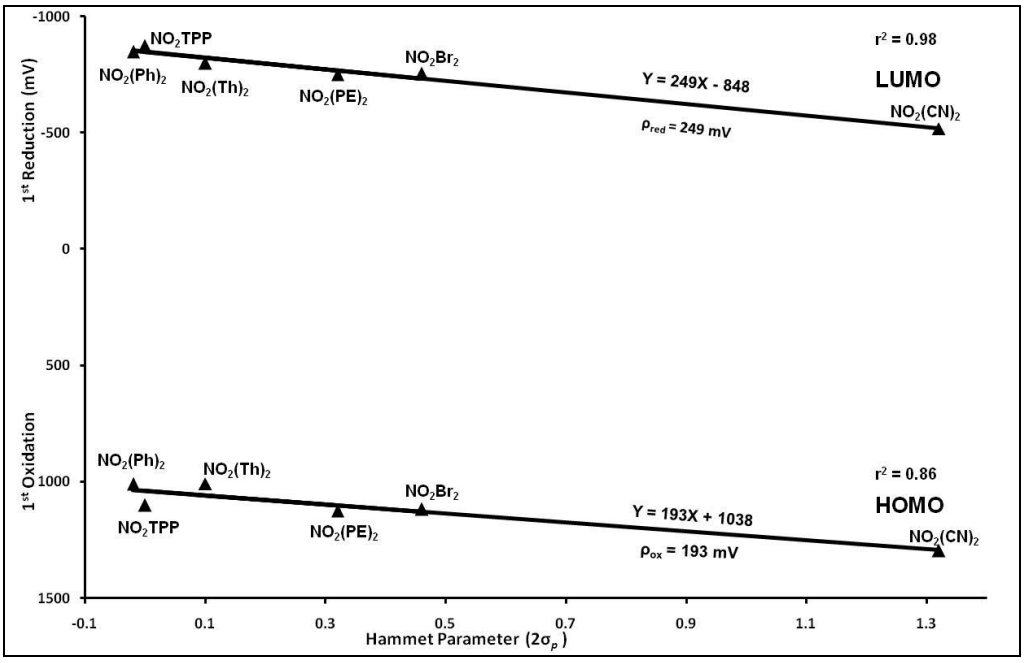
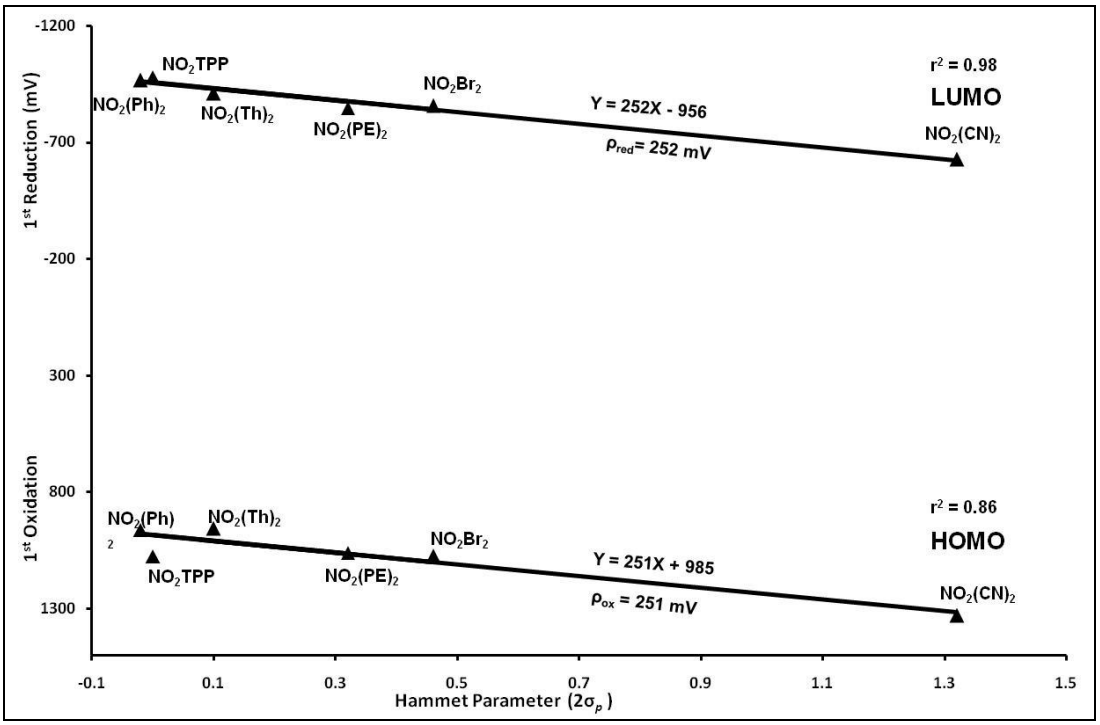


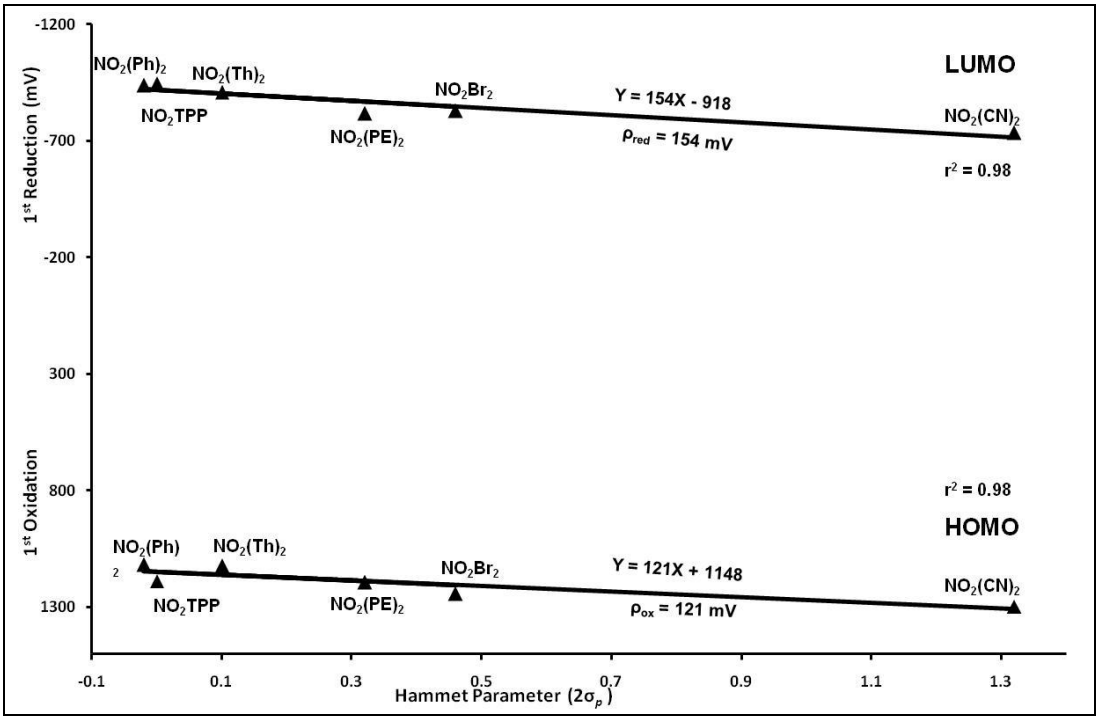
Figure S38. Plot of 1st ring redox potentials *versus* the Hammett parameter (σ_p) of various Mixed substituted Porphyrins.**(a)**H_2TPP(NO_2)X_2



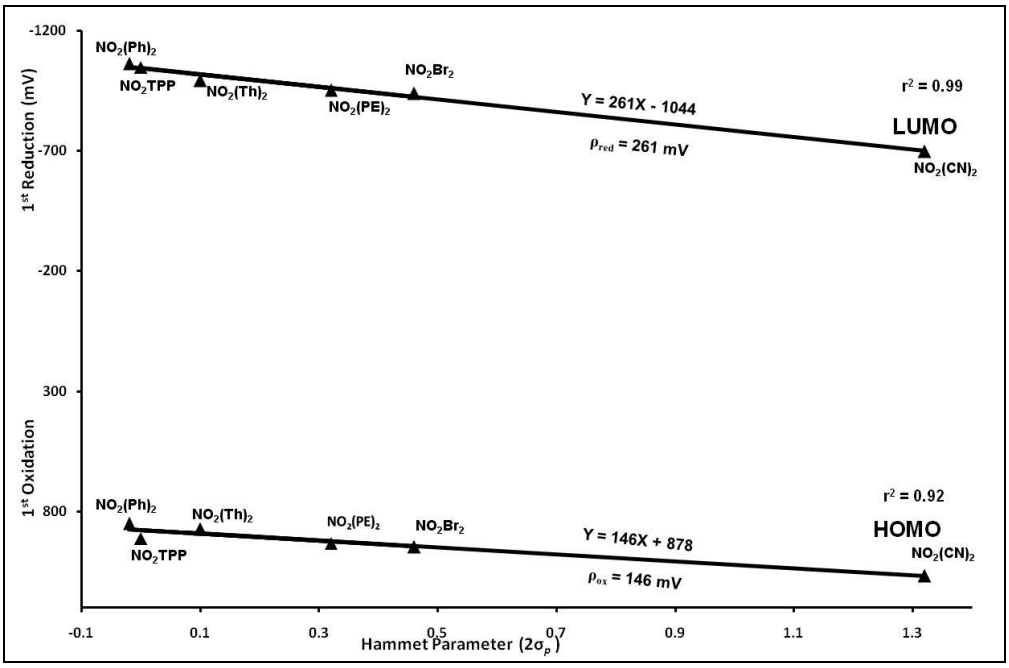
(b) $CuTPP(NO_2)X_2$



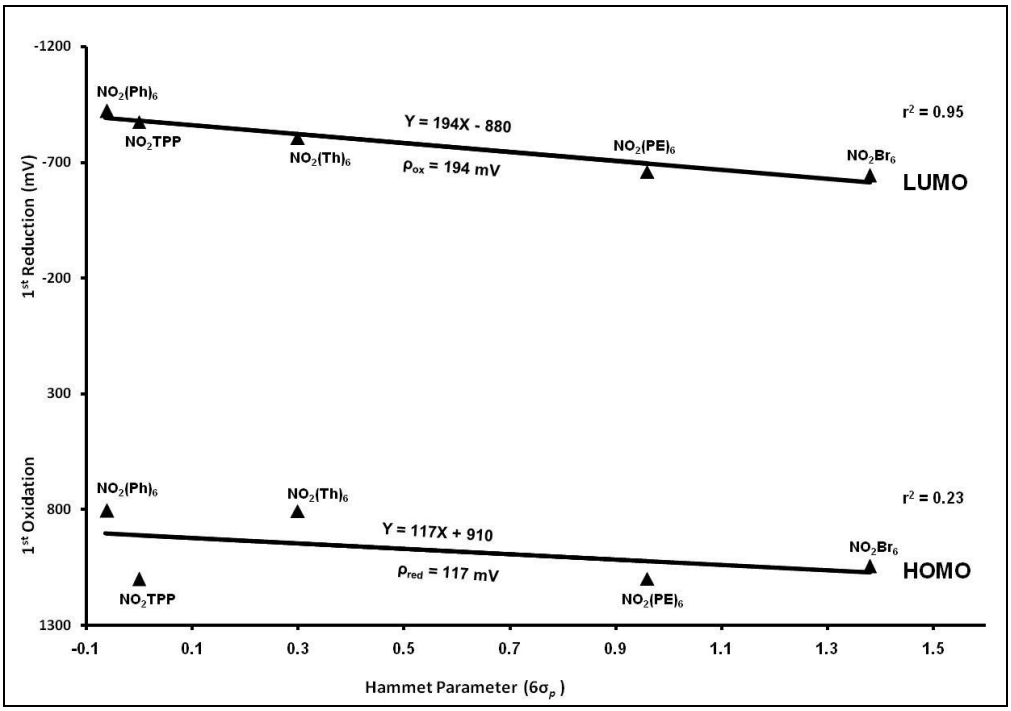
(c) $NiTPP(NO_2)X_2$



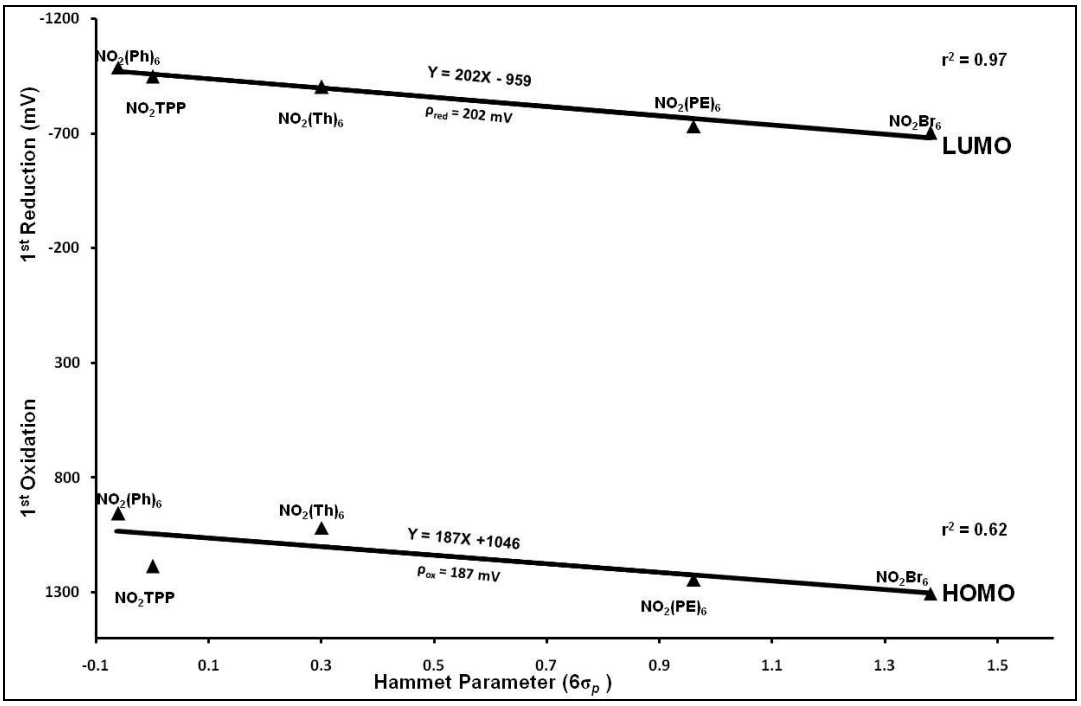
(d) $ZnTPP(NO_2)X_2$



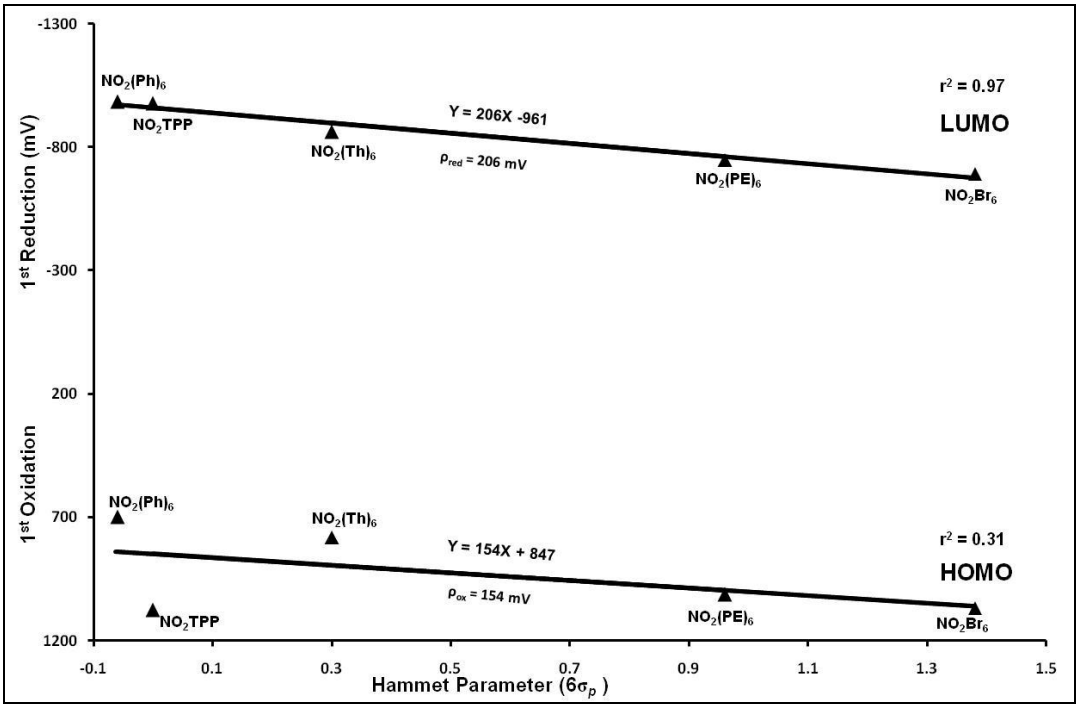
(e) $H_2TPP(NO_2)X_6$



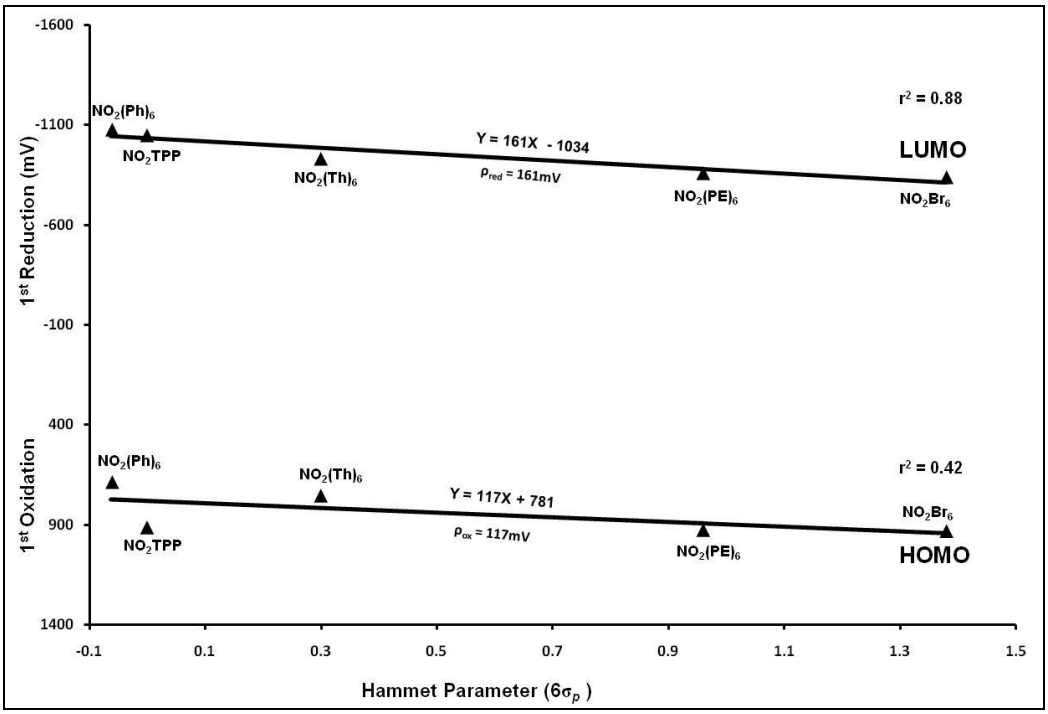
(f) $NiTPP(NO_2)X_6$



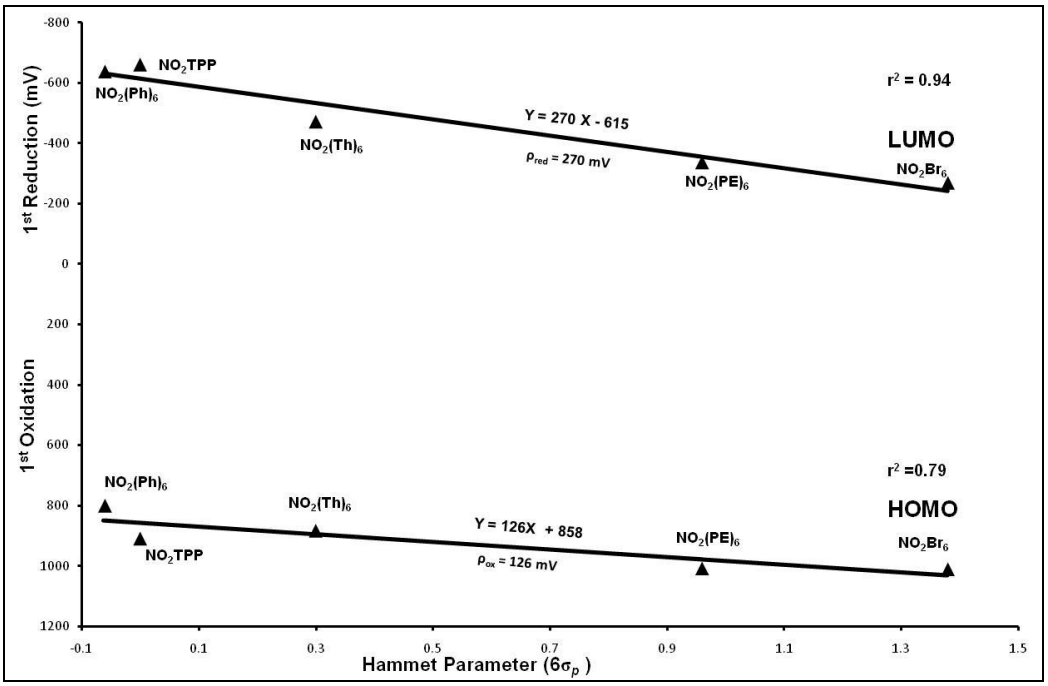
(g) $CuTPP(NO_2)X_6$



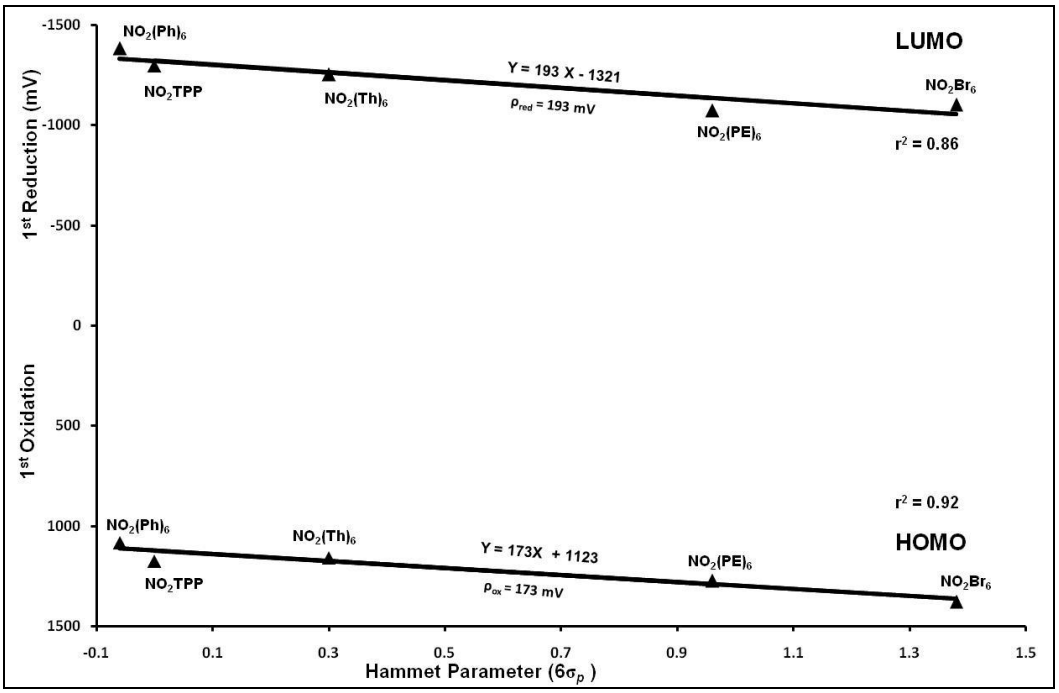
(h) $ZnTPP(NO_2)X_6$



(i) $CoTPP(NO_2)X_6$ (metal centered)



(j) $CoTPP(NO_2)X_6$ (ring centered)



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