Electronic Supplementary Information (ESI) for

Unsymmetrical Nonplanar 'Push-Pull' β-Octasubstituted Porphyrins: Facile Synthesis, Structural, Photophysical and Electrochemical Redox Properties

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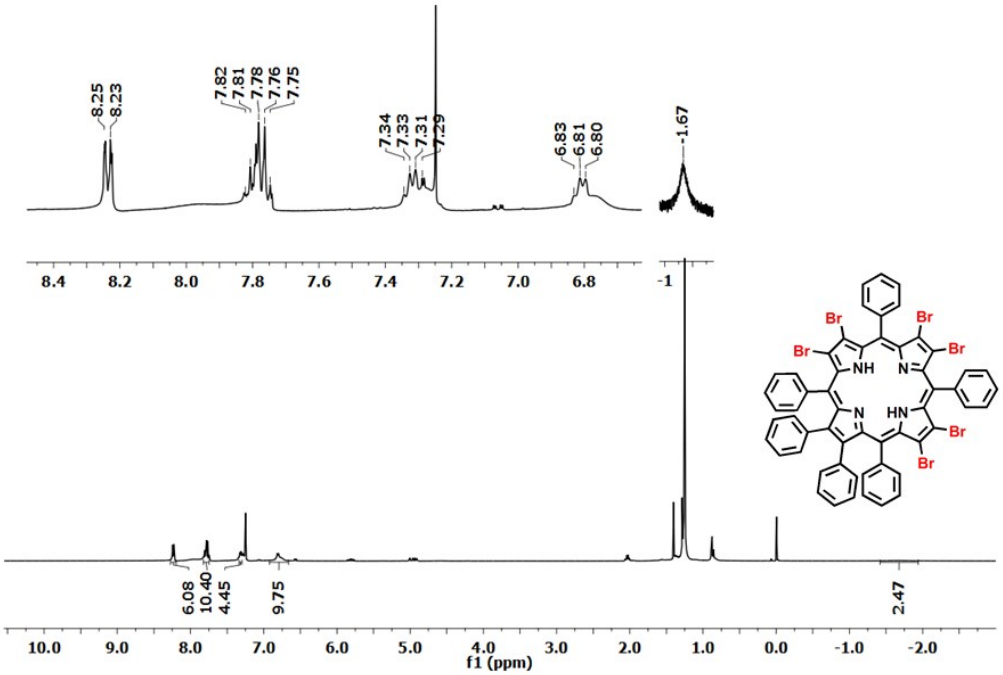


Figure S1. ^{1}H NMR $H_2TPP(Ph)_2Br_6$ in $CDCl_3$ at 298K.

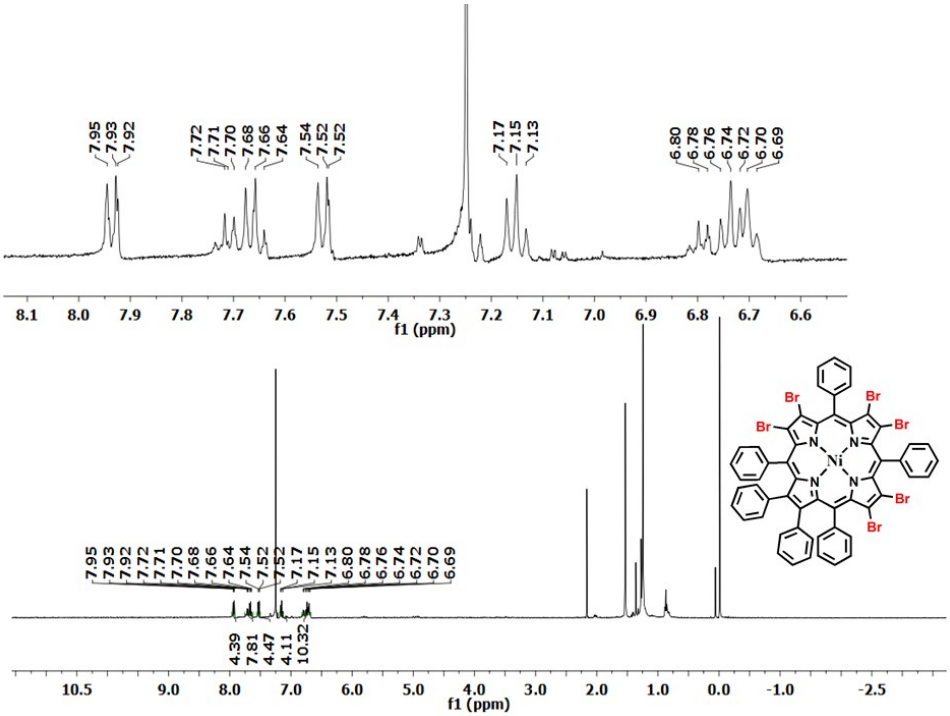


Figure S2. ^{1}H NMR $NiTPP(Ph)_2Br_6$ in $CDCl_3$ at 298K.

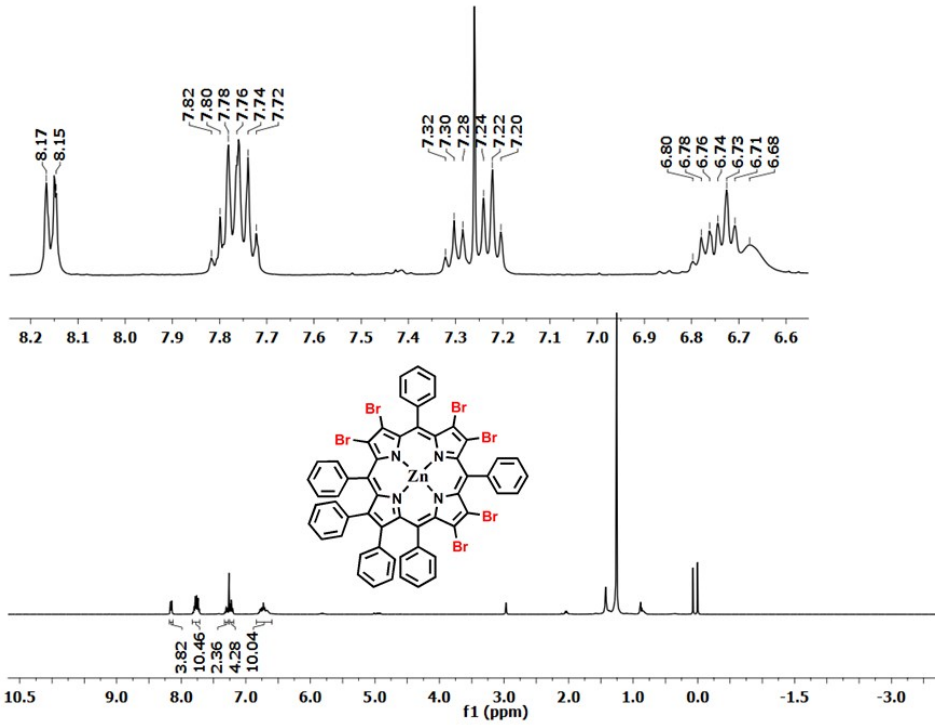


Figure S3. ^{1}H NMR $ZnTPP(Ph)_2Br_6$ in $CDCl_3$ at 298K.

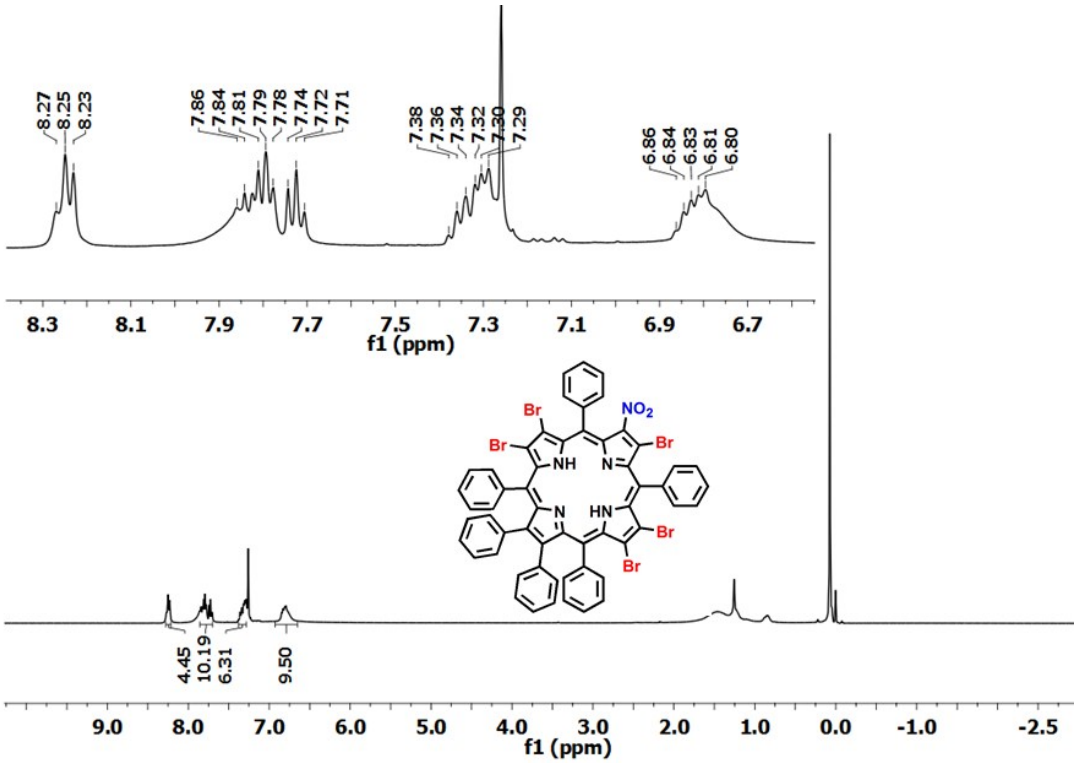


Figure S4. ^{1}H NMR spectrum of $H_2TPP(NO_2)(Ph)_2Br_5$ in $CDCl_3$ at 298 K.

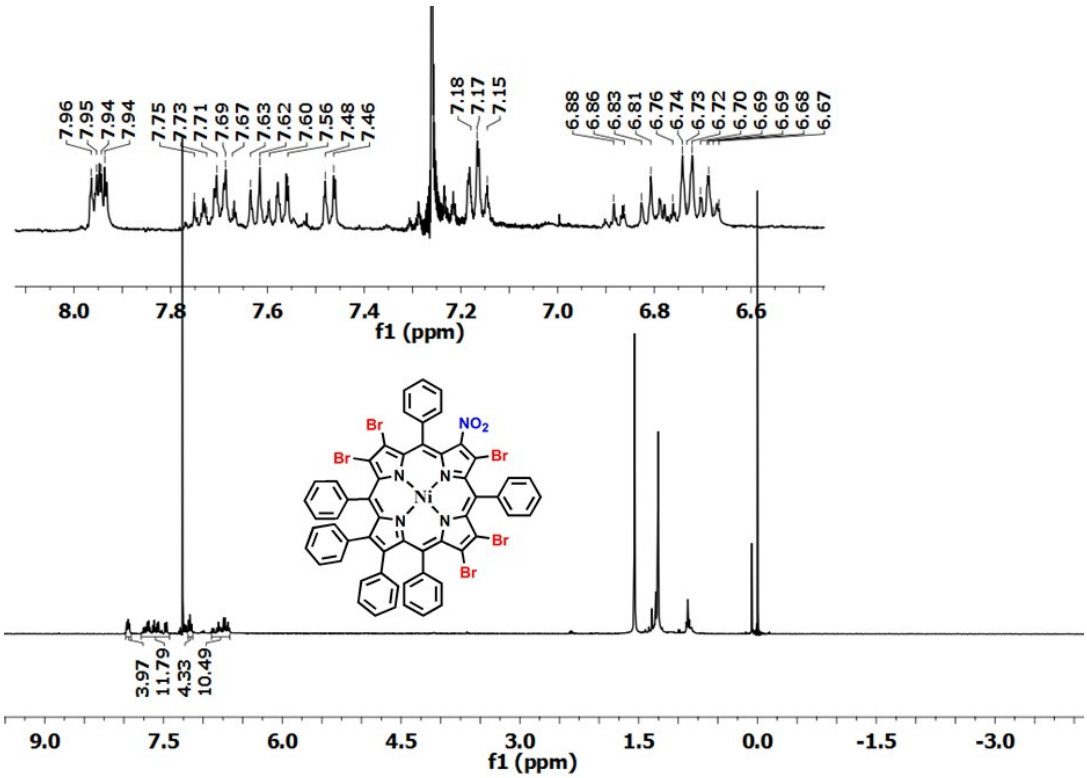


Figure S5. ^{1}H NMR spectrum of NiTPP(NO_2)$(Ph)_2Br_5$ in $CDCl_3$ at 298 K.

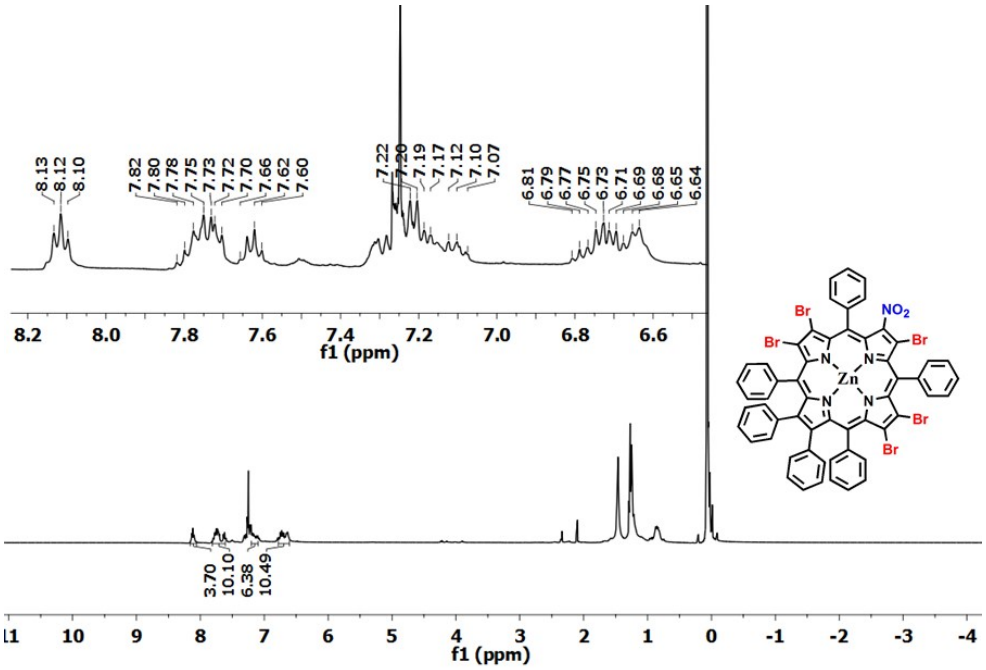


Figure S6. ^{1}H NMR spectrum of ZnTPP(NO_2)$(Ph)_2Br_5$ in $CDCl_3$ at 298 K.

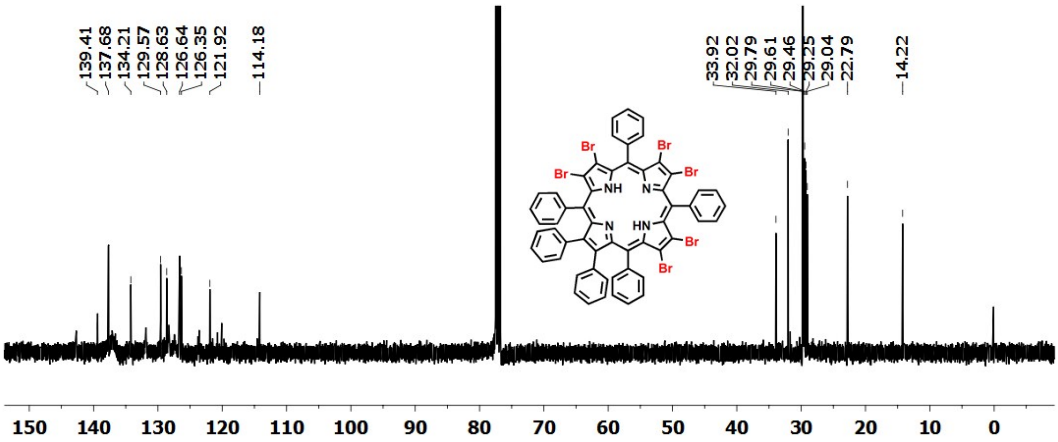


Figure S7. ^{13}C NMR spectrum of $H_2TPP(Ph)_2Br_6$ in $CDCl_3$ at 298 K.

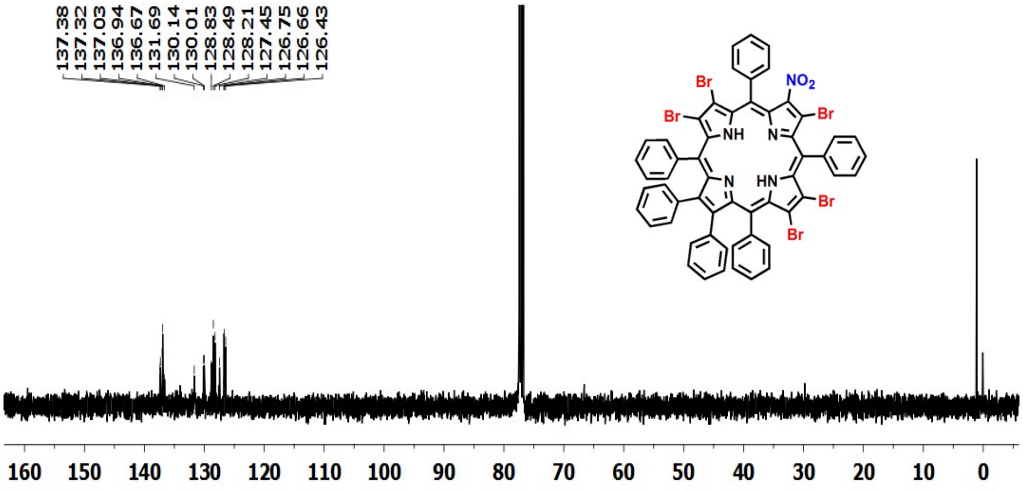


Figure S8. ^{13}C NMR spectrum of $H_2TPP(NO_2)(Ph)_2Br_5$in $CDCl_3$ at 298 K.

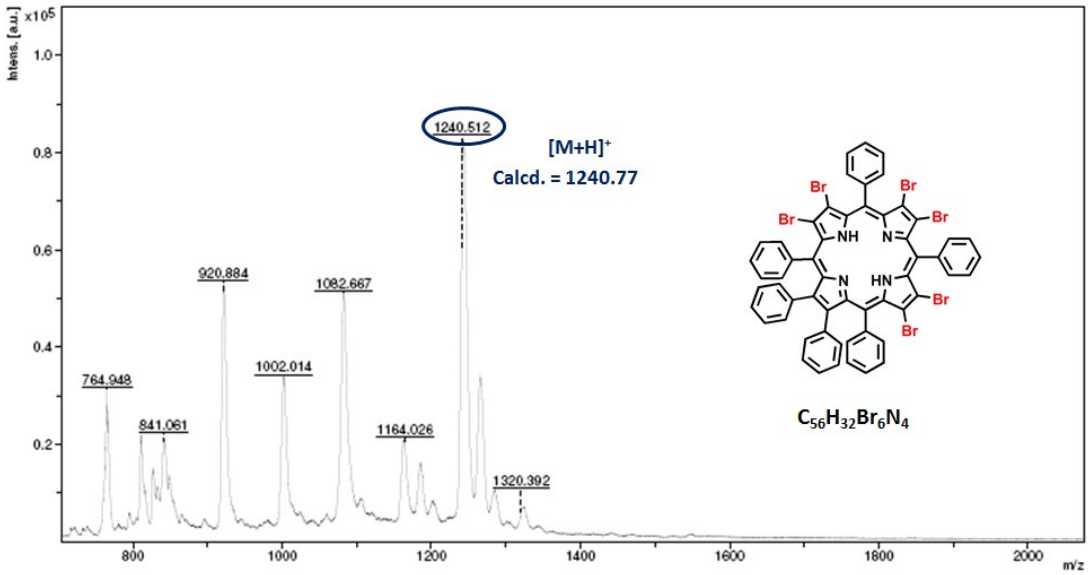


Figure S9. MALDI-TOF mass spectrum of $H_2TPP(Ph)_2Br_6$

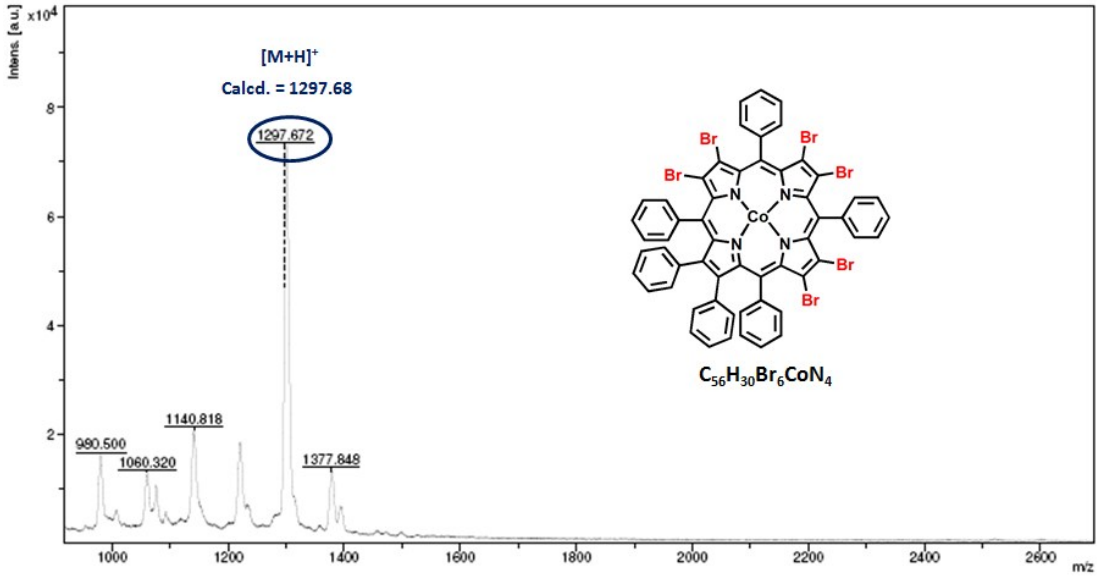


Figure S10. MALDI-TOF mass spectrum of $CoTPP(Ph)_2Br_6$.

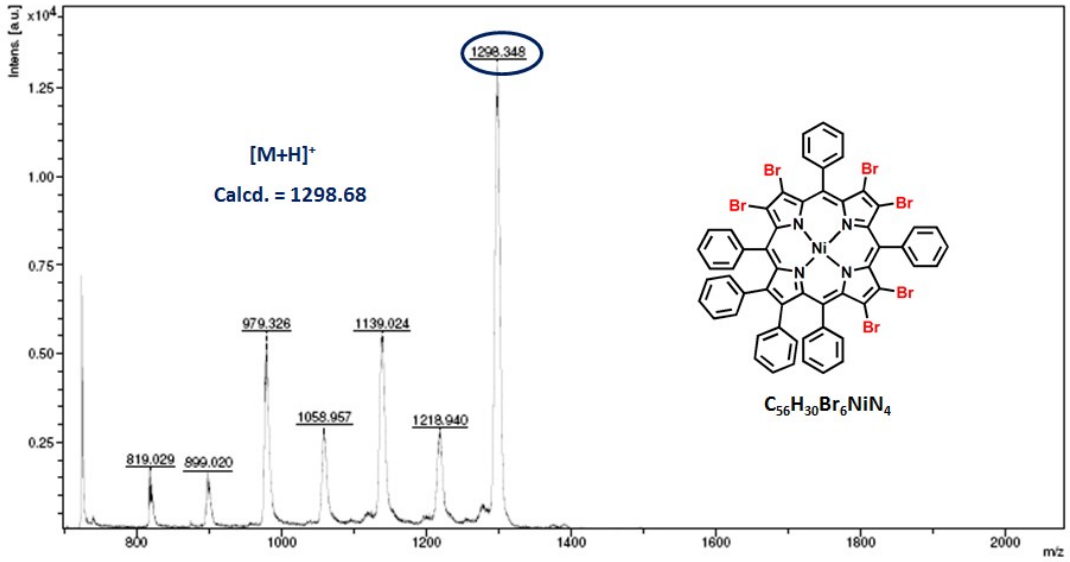


Figure S11. MALDI-TOF mass spectrum of $NiTPP(Ph)_2Br_6$.

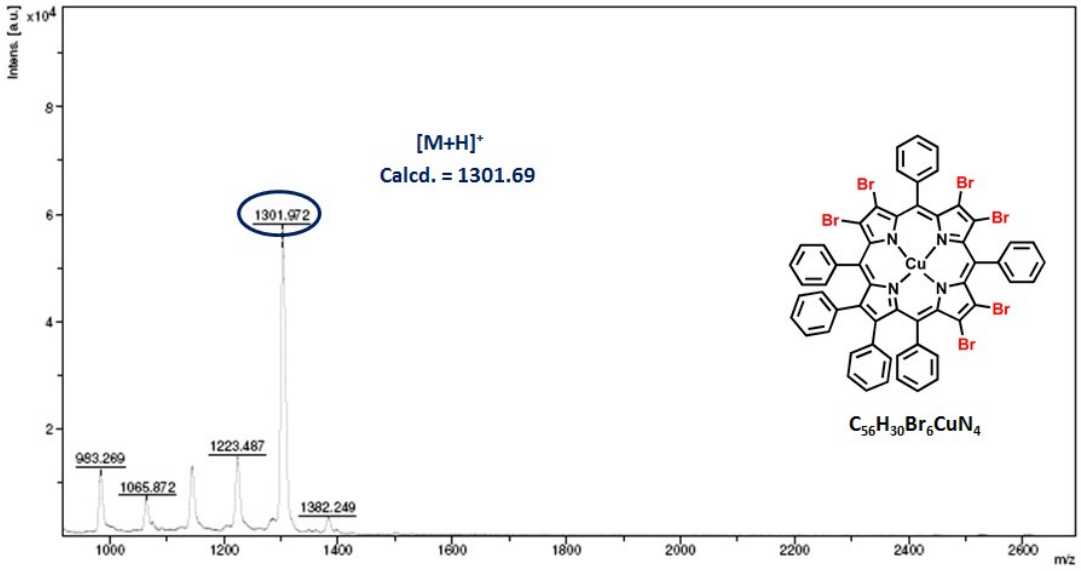


Figure S12. MALDI-TOF mass spectrum of $CuTPP(Ph)_2Br_6$.

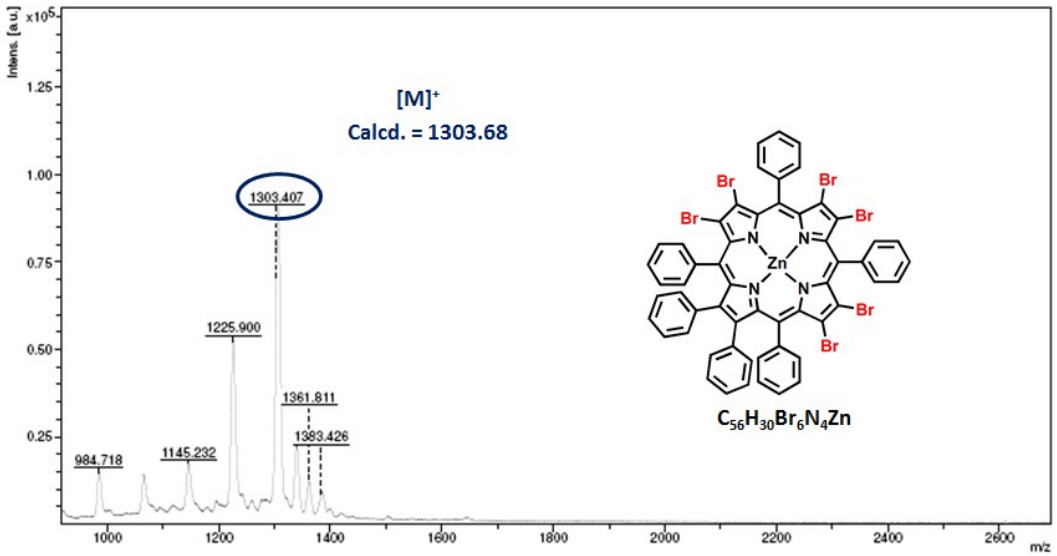


Figure S13. MALDI-TOF mass spectrum of $ZnTPP(Ph)_2Br_6$.

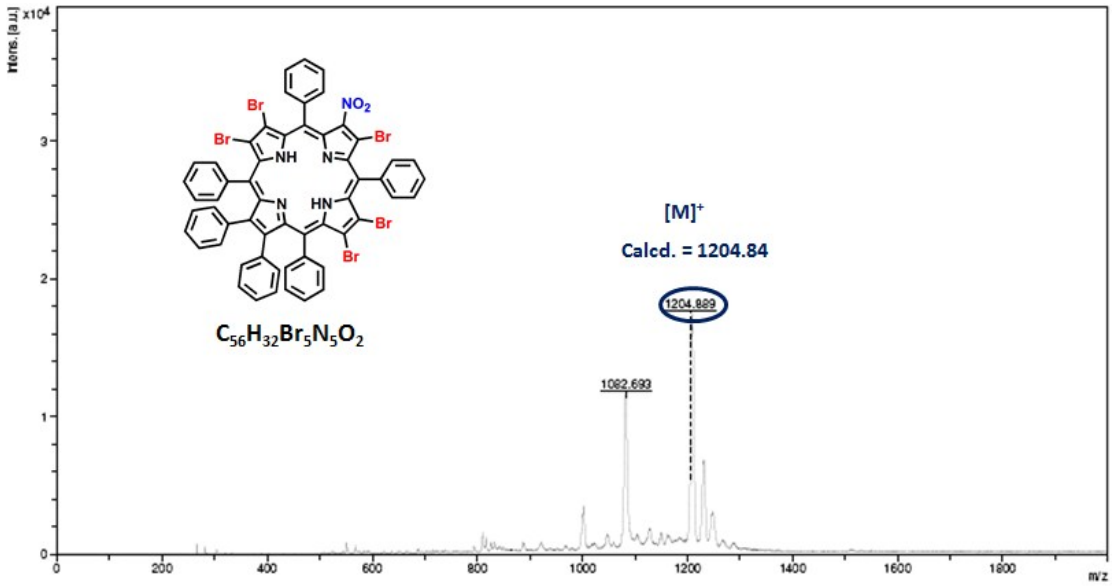


Figure S14. MALDI-TOF mass spectrum of $H_2TPP(NO_2)(Ph)_2Br_5$.

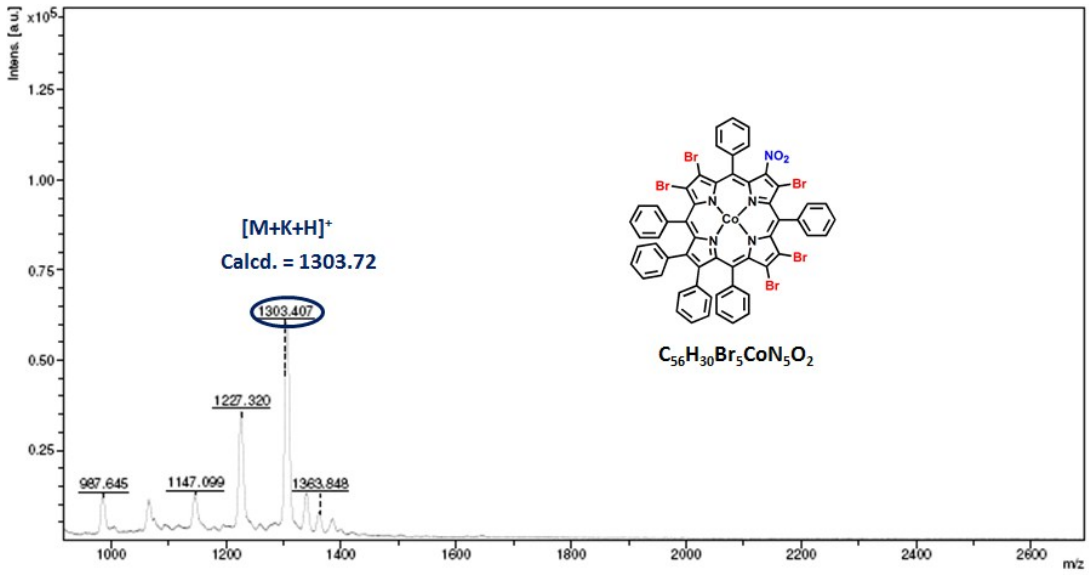


Figure S15. MALDI-TOF mass spectrum of CoTPP(NO_2)$(Ph)_2Br_5$.

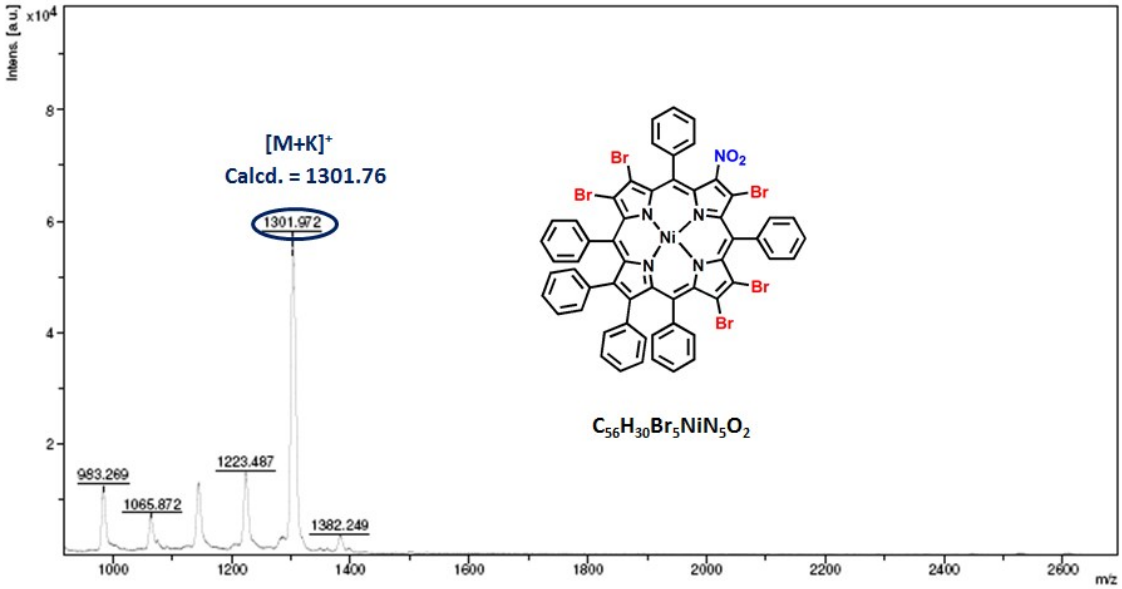


Figure S16. MALDI-TOF mass spectrum of NiTPP(NO_2)$(Ph)_2Br_5$.

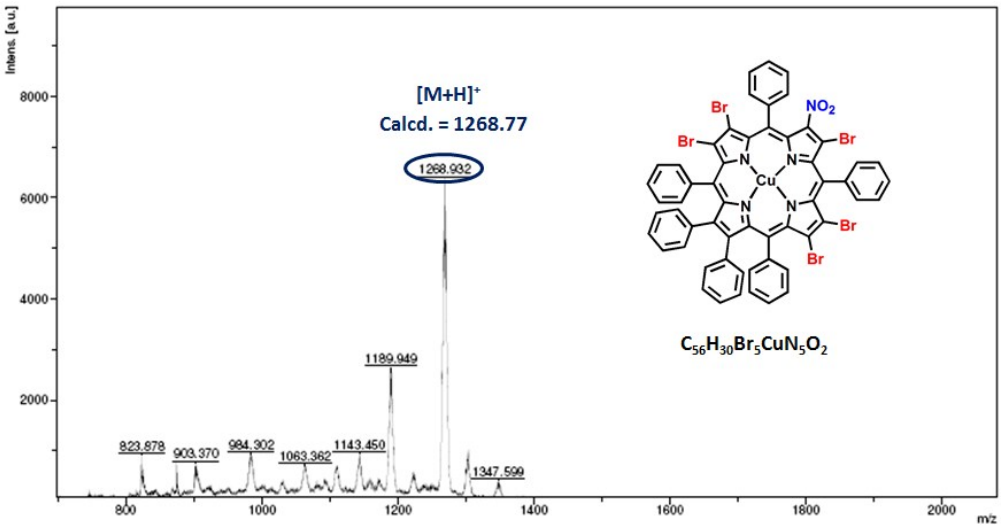


Figure S17. MALDI-TOF mass spectrum of $CuTPP(NO_2)(Ph)_2Br_5$.

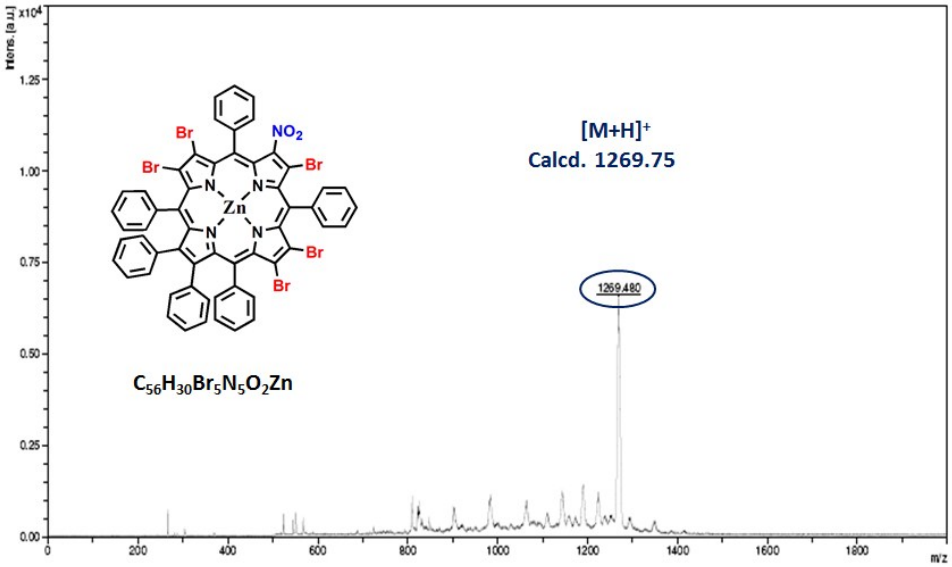


Figure S18. MALDI-TOF mass spectrum of $ZnTPP(NO_2)(Ph)_2Br_5$.

Table S1. Crystalographic data of $H_2TPP(NO_2)(Ph)_2Br_5$	
	$H_2TPP(NO_2)(Ph)_2Br_5$
Emperical Formula	C58H40Br5N5O4
Formula wt.	1270.50
Crystal system	Monoclinic
Space group	P 21/c
a (Å)	13.7272(4) Å
b (Å)	27.1133(10) Å
c (Å)	14.7309(5) Å
α (˚)	90
β (˚)	101.409(2)
γ (˚)	90
Volume ($Å^3$)	5374.4(3) $Å^3$
Z	4
Dcald (mg/m^3)	1.570 mg/m^3
λ (Å)	0.71073 Å
T (^0C)	296(2) K
No. of total reflns.	72230
No. of indepnt. reflns.	9721
R	0.1082
R_w	0.1638
GOOF	1.027
CCDC No.	1921730

Table S2. Selected average bond lengths (Å) and bond angles (°) for the single crystal of $H_2TPP(NO_2)(Ph)_2Br_5$.	
Bond Length(Å)	
	$H_2TPP(NO_2)(Ph)_2Br_5$
$N-C_{\alpha}$	1.354
$N'-C_{\alpha'}$	1.311
$C_{\alpha}-C_{\beta}$	1.428
$C_{\alpha'}-C_{\beta'}$	1.465
$C_{\beta}-C_{\beta}$	1.366
$C_{\beta'}-C_{\beta'}$	1.273
$C_{\alpha}-C_{m}$	1.411
$C_{\alpha'}-C_{m}$	1.332
ΔC_{β} (Å)	**1.23**
Δ24 (Å)	**0.558**
Bond Angle (deg)	
$N-C_{\alpha}-C_{m}$	125.42
$N'-C_{\alpha'}-C_{m}$	119.01
$N-C_{\alpha}-C_{\beta}$	106.88
$N'-C_{\alpha'}-C_{\beta'}$	111.35
$C_{\beta}-C_{\alpha}-C_{m}$	127.53
$C_{\beta'}-C_{\alpha'}-C_{m}$	129.60
$C_{\alpha}-C_{m}-C_{\alpha'}$	123.34
$C_{\alpha}-C_{\beta}-C_{\beta}$	107.63
$C_{\alpha'}-C_{\beta'}-C_{\beta'}$	106.01
$C_{\alpha}-N-C_{\alpha}$	110.94
$C_{\alpha'}-N'-C_{\alpha'}$	105.16

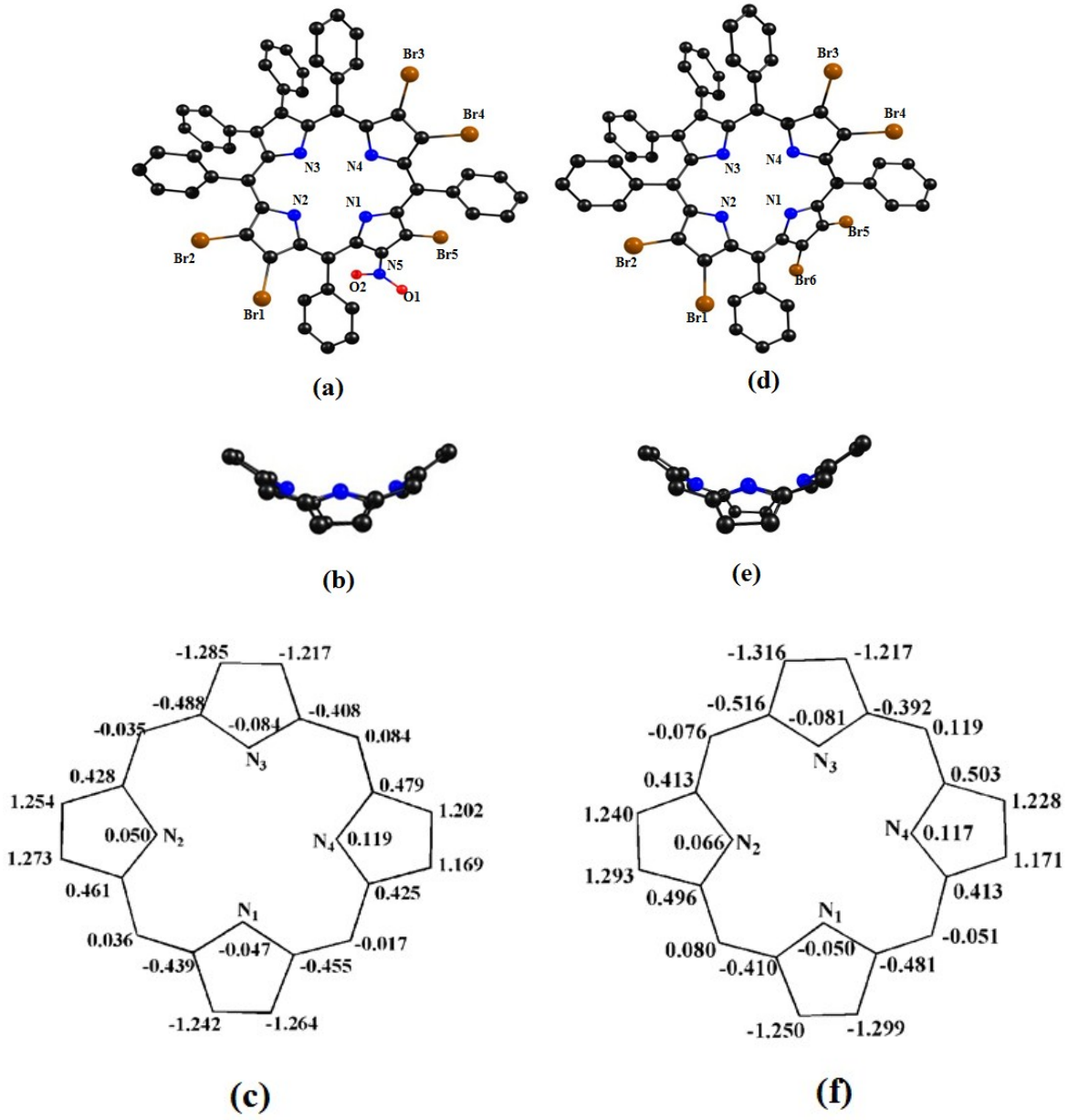
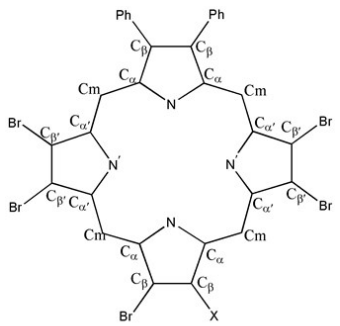


Figure S19. B3LYP/LANL2DZ- optimized geometry showing the Top views as well as side views of $H_2TPP(NO_2)(Ph)_2Br_5$ (1a and 1b) and $H_2TPP(Ph)_2Br_6$ (1d and 1e) respectively. The displacement of porphyrin-core atoms from mean plane are shown in figures 1c and 1f for $H_2TPP(NO_2)(Ph)_2Br_5$ and $H_2TPP(Ph)_2Br_6$ respectively.



X = NO_2, Br

Table S3. Selected bond lengths (Å) and bond angles (°) for the B3LYP/LANL2DZ optimized geometries of $H_2TPP(Ph)_2Br_5X$ (X = NO_2 or Br).

	$H_2TPP(Ph)_2Br_6$	**$H_2TPP(NO_2)(Ph)_2Br_5$**
	Bond Length (Å)	
N-C_α	1.385	1.384
N′-$C_{\alpha'}$	1.391	1.391
C_α-C_β	1.477	1.475
$C_{\alpha'}$-$C_{\beta'}$	1.450	1.451
C_β-C_β	1.382	1.384
$C_{\beta'}$-$C_{\beta'}$	1.393	1.391
C_α-C_m	1.426	1.427
$C_{\alpha'}$-C_m	1.420	1.418
ΔC_β (Å)	**1.251**	**1.238**
Δ24 (Å)	**0.594**	**0.581**
	Bond Angle (deg)	
N-C_α-C_m	**122.80**	**123.13**
N′-$C_{\alpha'}$-C_m	123.45	123.45
N-C_α-C_β	109.64	109.64
N′-$C_{\alpha'}$-$C_{\beta'}$	105.05	105.09
C_β-C_α-C_m	**127.26**	**118.81**
$C_{\beta'}$-$C_{\alpha'}$-C_m	131.43	131.31
C_α-C_m-$C_{\alpha'}$	121.90	121.84
C_α-C_β-C_β	106.59	106.58
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	108.51	108.50
C_α-N- C_α	106.89	107.00
$C_{\alpha'}$-N′- $C_{\alpha'}$	112.47	112.41

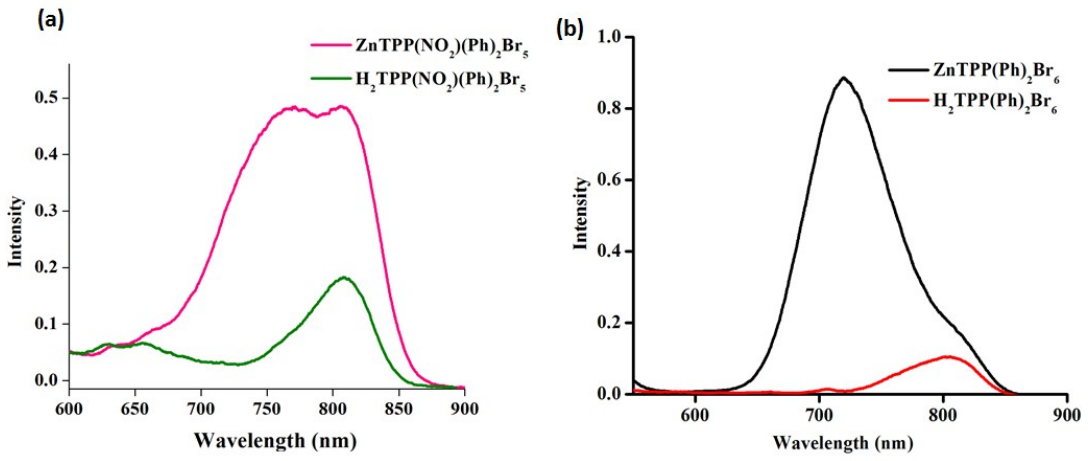


Figure S20. Fluorescence spectra of (a) $MTPP(NO_2)(Ph)_2Br_5$ and (b) $MTPP(Ph)_2Br_6$ (M = 2H, Zn (II)) in CH_2Cl_2 at 298 K

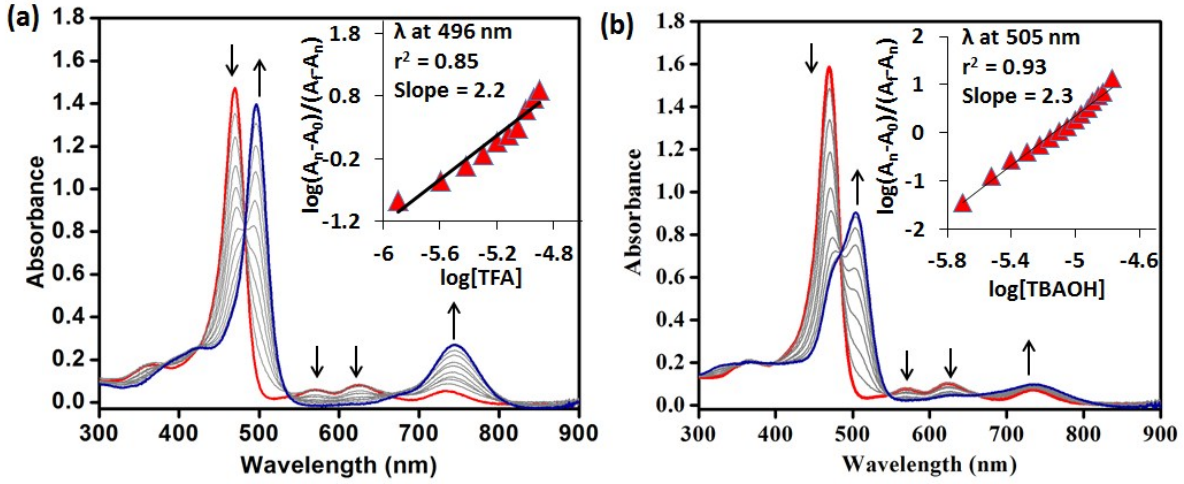


Figure S21. UV-visible spectral titration of $H_2TPP(Ph)_2Br_6$ with TFA (a) and TBAOH (b) in toluene at 298 K respectively. insets shows the corresponding Hill plots.

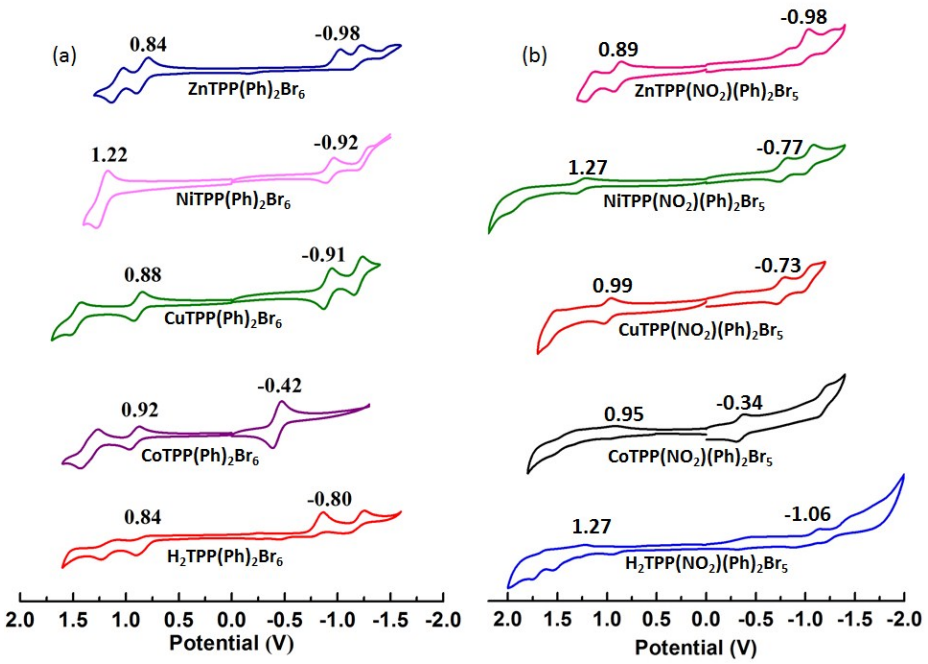


Figure S22. Cyclic Voltametric (in V vs Ag/ AgCl) traces recorded for porphyrins (**a**) $MTPP(Ph)_2Br_6$(M = 2H, Co(II), Cu(II), Ni(II), Zn(II)) and (**b**) $MTPP(NO_2)(Ph)_2Br_5$ (M = 2H, Co(II), Cu(II), Ni(II), Zn(II)) in CH_2Cl_2 containing 0.1 M $TBAPF_6$ with a scan rate of 0.1 V/s at 298 K.