Electronic Supplementary Information

β-Methoxyphenyl Substituted Porphyrins: Synthesis, Characterization and Comprehensive Spectral, Structural, Electrochemical and Theoretical Analysis

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Figure S12. 2D-fingerprint plots showing relative contribution of different types of interactions between atoms in crystal packing of CuTPP(m-CH$_3$O-Ph)$_2$.The di and de values are the closest internal and external distances (in A°) from given points on the hirshfeld surface of CuTPP(m-CH$_3$O-Ph)$_2$.

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Table S1. Optical absorption spectral data of all the newly synthesized β-di-substituted free base porphyrins as well as their metal complexes functionalized with mono-, di- & tri-substituted methoxyphenyl groups. The values in parentheses refer to log ε (ε in dm^3 mol^{-1} cm^{-1}.

Porphyrins	Soret band, (nm)	Q band(s), (nm)
H$_2$TPP(p-OCH$_3$-Ph)$_2$	425 (5.58)	522 (4.34), 554 (4.02), 594 (3.61), 650 (3.47)
CuTPP(p-OCH$_3$-Ph)$_2$	418 (5.58)	537 (4.13)
CoTPP(p-OCH$_3$-Ph)$_2$	421 (5.63)	545 (4.39)
NiTPP(p-OCH$_3$-Ph)$_2$	424 (5.63)	539 (4.48)
ZnTPP(p-OCH$_3$-Ph)$_2$	425 (5.62)	553 (4.35),589 (3.71)
H$_2$TPP(m-OCH$_3$-Ph)$_2$	423 (5.57)	521 (4.32), 557 (4.21) 592 (4.00), 653 (3.47)
CuTPP(m-OCH$_3$-Ph)$_2$	421 (5.66)	544 (4.25)
CoTPP(m-OCH$_3$-Ph)$_2$	417 (5.62)	536 (4.57)
NiTPP(m-OCH$_3$-Ph)$_2$	420 (5.63)	535 (4.49)
ZnTPP(m-OCH$_3$-Ph)$_2$	423 (5.60)	552 (4.31), 594 (3.70)
H$_2$TPP(m,p-OCH$_3$-Ph)$_2$	421 (5.62)	518 (4.39), 553 (4.19), 593 (3.90), 648 (3.64)
CuTPP(m,p-OCH$_3$-Ph)$_2$	417 (5.64)	542 (4.38)
CoTPP(m,p-OCH$_3$-Ph)$_2$	414 (5.59)	532 (4.53)
NiTPP(m,p-OCH$_3$-Ph)$_2$	423 (5.61)	538 (4.46)
ZnTPP(m,p-OCH$_3$-Ph)$_2$	422 (5.65)	551 (4.37), 592 (3.67)
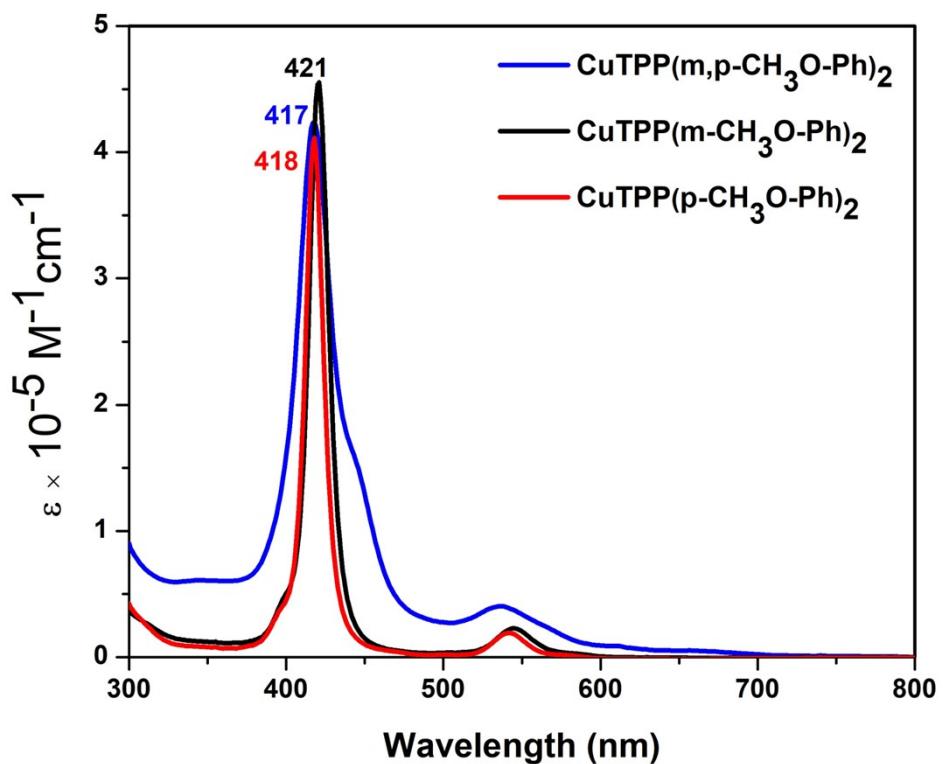
Figure S1. UV- Visible spectra of CuTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in CH$_2$Cl$_2$.
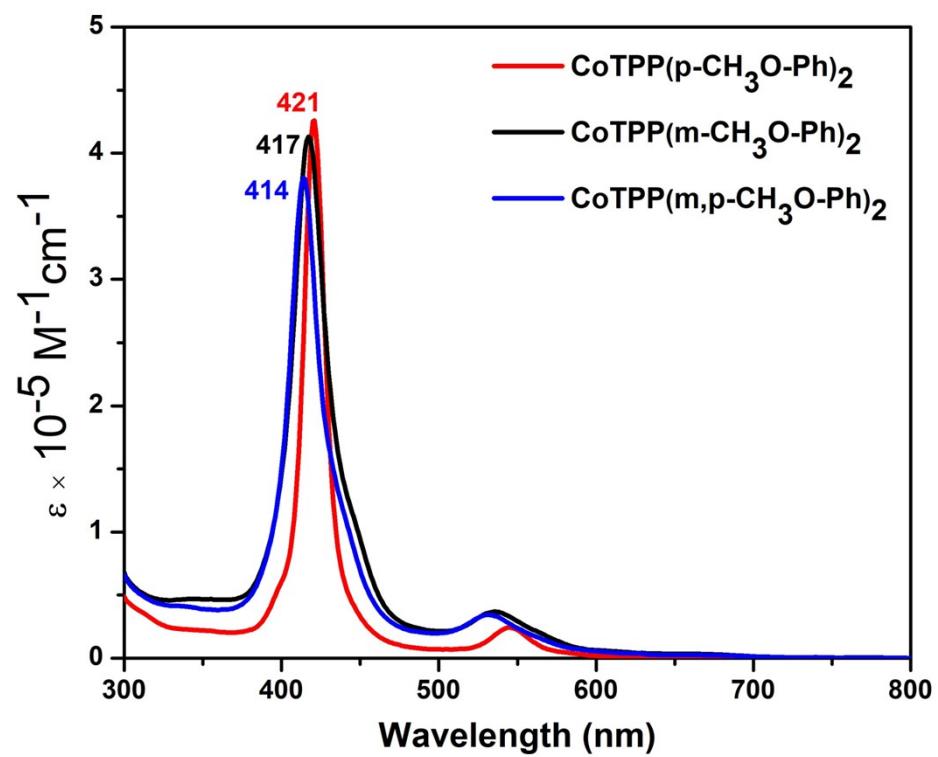
Figure S2. UV- Visible spectra of CoTPP(R)$_2$; where R = p-CH$_3$O-Ph, m-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in CH$_2$Cl$_2$.
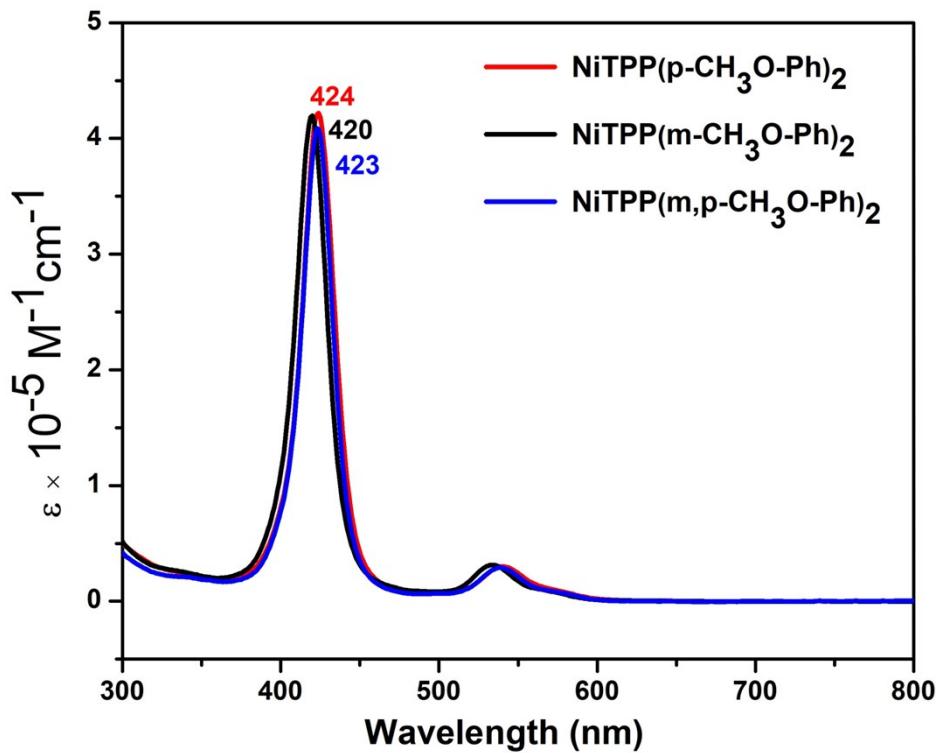
Figure S3. UV- Visible spectra of CoTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in CH$_2$Cl$_2$.
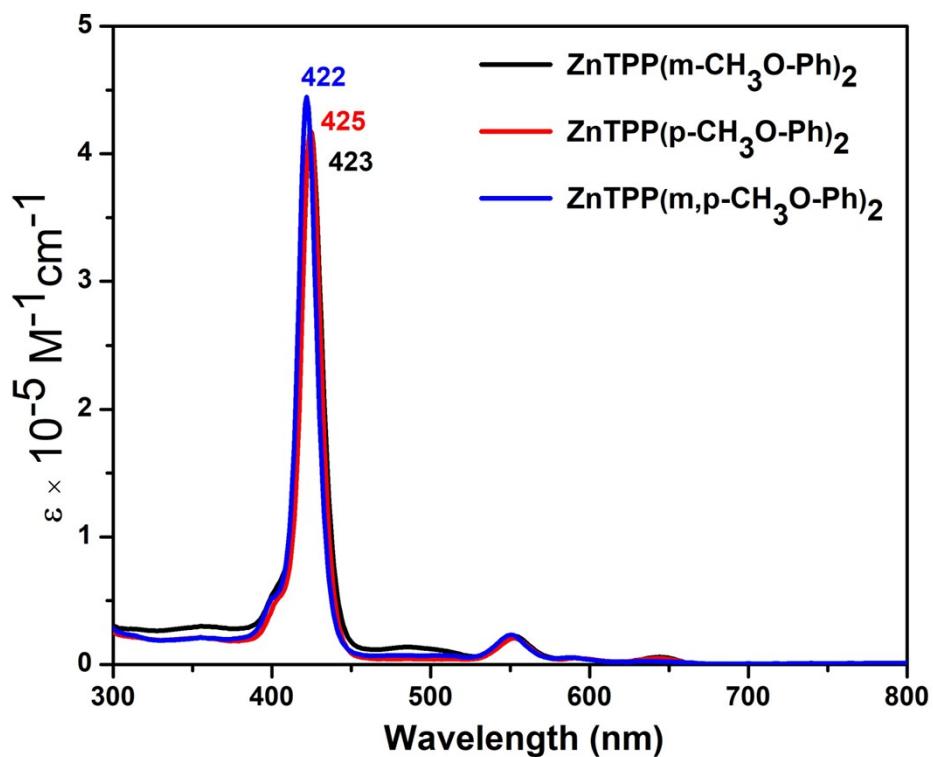
Figure S4. UV- Visible spectra of CoTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in CH$_2$Cl$_2$.

Table S2. Fluorescence spectral data of ZnTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph derivatives in CH$_2$Cl$_2$ at 298 K, (Φ_f = quantum yield relative to those of ZnTPP in DCM).

Porphyrins	λ excitation, nm	λ emission, nm	Φ_f
ZnTPP(*p*-OCH$_3$-Ph)$_2$	424	657	0.0088
ZnTPP(*m*-OCH$_3$-Ph)$_2$	423	656	0.0097
ZnTPP(*m,p*-OCH$_3$-Ph)$_2$	422	654	0.0095
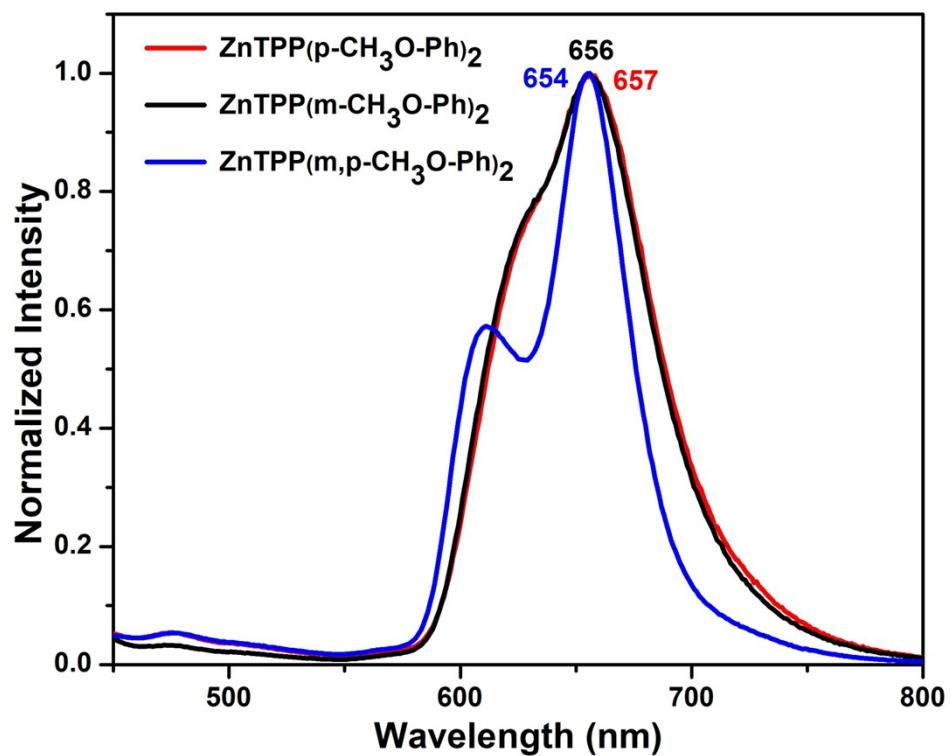
Figure S5. Fluorescence spectra of ZnTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in CH$_2$Cl$_2$ at 298 K.

Table S3. Electrochemical redox data of newly synthesized free base β-tri-substituted porphyrins functionalized with mono-, di- & tri-substituted methoxyphenyl groups and their metal complexes MTPP(R)$_2$; where M = H$_2$, Cu(II), Ni(II) & Zn(II) and R = p-CH$_3$O-Ph, m-CH$_3$O-Ph & m,p-CH$_3$O-Ph (in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ with a scan rate of 0.1 V/s at 298 K).

Porphyrins	Oxidation (V)			Reduction (V)			ΔE (V)
	I-Oxd	II-Oxd	III-Oxd	I-Red	II-Red	III-Red	
H$_2$TPP(p-OCH$_3$-Ph)$_2$	0.90	1.08		-1.19	-1.65[a]		2.08
CuTPP(p-OCH$_3$-Ph)$_2$	0.86	1.25		-1.31	-1.67[a]		2.17
CoTPP(p-OCH$_3$-Ph)$_2$	0.65	1.06	1.23	-0.73a	-1.31	-1.39 [a]	2.37
NiTPP(p-OCH$_3$-Ph)$_2$	0.95	1.23		-1.27	-1.87 [a]		2.22
ZnTPP(p-OCH$_3$-Ph)$_2$	0.76	0.98		-1.37	-1.62 [a]		2.13
H$_2$TPP(m-OCH$_3$-Ph)$_2$	0.94	1.09[a]		-1.19	-1.41		2.13
CuTPP(m-OCH$_3$-Ph)$_2$	0.88	1.32	1.51	-1.29	-1.67 [a]		2.17
CoTPP(m-OCH$_3$-Ph)$_2$	0.71	1.09	1.37	-0.84	-1.15	-1.38	2.24
NiTPP(m-OCH$_3$-Ph)$_2$	1.03	1.29	1.46	-1.11	-1.31	-1.71	2.14
ZnTPP(m-OCH$_3$-Ph)$_2$	0.80	1.03		-1.36	-1.58[a]		2.17
H$_2$TPP(m,p-OCH$_3$-Ph)$_2$	1.01	1.24	1.47	-1.22	-1.52 [a]		2.22
CuTPP(m,p-OCH$_3$-Ph)$_2$	0.95	1.31	1.46	-1.12	-1.35		2.01
CoTPP(m,p-OCH$_3$-Ph)$_2$	0.82	1.08	1.27	-0.84	-1.16	-1.41	2.24
NiTPP(m,p-OCH$_3$-Ph)$_2$	0.99	1.27	1.46	-1.32	-1.76	-1.95[a]	2.31
ZnTPP(m,p-OCH$_3$-Ph)$_2$	0.83	1.09	1.45	-1.35	-1.57		2.18

[a]refers to the values taken from DPV experiment
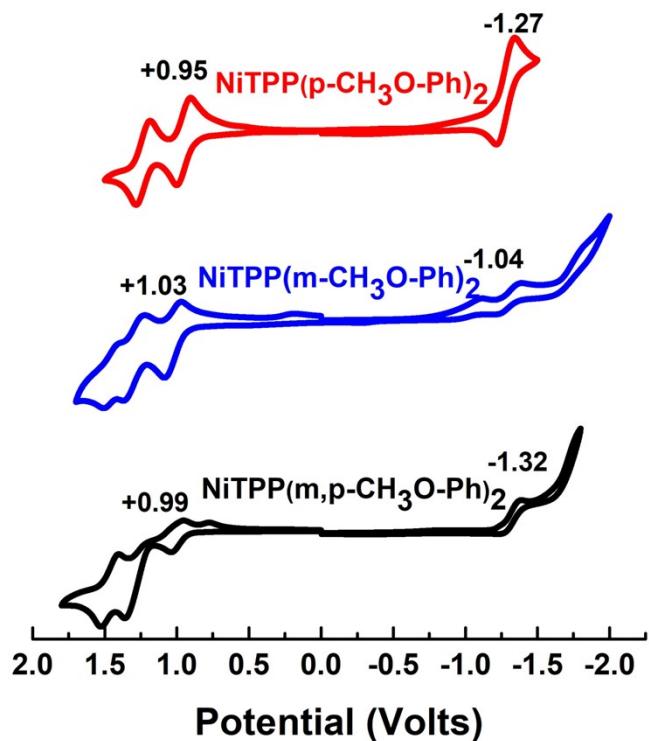
Figure S6. Cyclic voltammograms of NiTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph (~1 mM) in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ using Ag/AgCl as reference electrode with a scan rate of 0.10 V/s at 298 K.
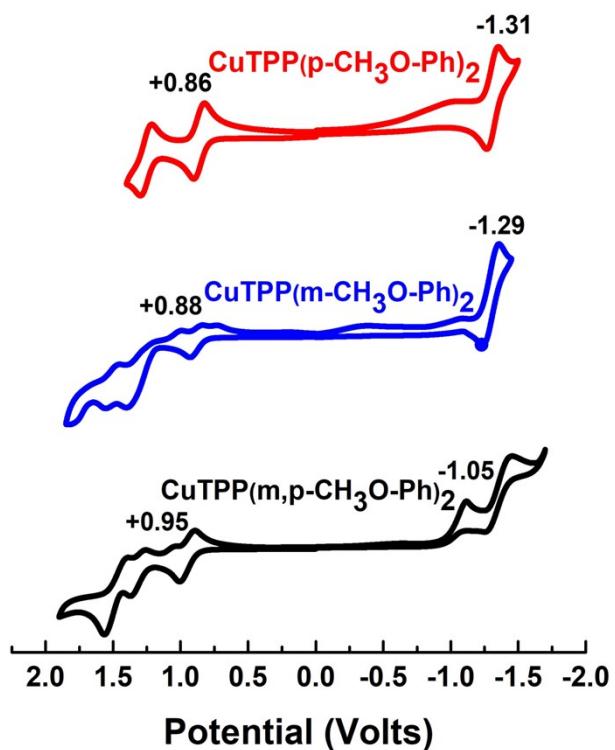
Figure S7. Cyclic voltammograms of CuTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, m-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph (~1 mM) in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ using Ag/AgCl as reference electrode with a scan rate of 0.10 V/s at 298 K.
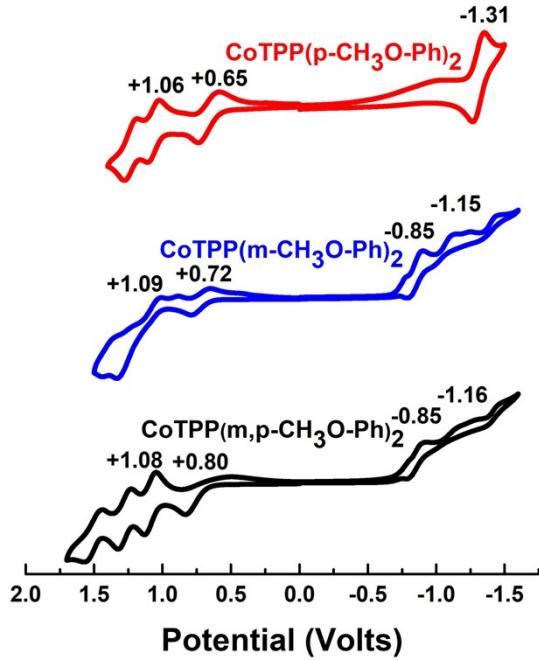
Figure S8. Cyclic voltammograms of CoTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph (~1 mM) in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ using Ag/AgCl as reference electrode with a scan rate of 0.10 V/s at 298 K.

	H$_2$TPP(*p*-CH$_3$O-Ph)$_2$	ZnTPP(*m*-CH$_3$O-Ph)$_2$	CuTPP(*m*-CH$_3$O-Ph)$_2$
Empirical formula	C$_{58}$H$_{42}$N$_4$O$_2$	C$_{65}$H$_{49}$N$_5$O$_4$Zn	C$_{60}$H$_{44}$N$_4$O$_4$Cu
Formula wt.	826.95	1029.46	948.53
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2$_1$/c	P-1
a (Å)	25.4032(11) Å	9.9765(3) Å	13.2014(7) Å
b (Å)	10.7091(5) Å	41.7796(16) Å	13.3397(7) Å
c (Å)	36.4314(15) Å	13.3216(5) Å	14.8686(7) Å
α (º)	90°	90°	65.629(2)°
β (º)	109.790(2)°	107.3030(10)	76.969(2)°
γ (º)	90°	90°	89.430(2)°
Volume (Å^3)	9325.6(7) Å^3	5301.3(3) Å^3	2313.5(2) Å^3
Z	8	4	2
D$_{calc}$ (Mg/m^3)	1.178 Mg/m^3	1.290 Mg/m^3	1.362 Mg/m^3
Wavelength (Å)	1.54178 Å	0.71073 Å	0.71073 Å
T (K)	296 (2) K	298 (2) K	298 (2) K
No. of total reflns.	62109	101253	99719
No. of indepnt.reflns.	8097	9304	10063
R[a]	0.0721	0.0892	0.0415
R[b]	0.1922	0.1759	0.0946
Theta range for data collection	2.578 to 66.492°.	2.894 to 22.000°.	2.876 to 26.994°.
Crystal size	0.540 x 0.051 x 0.023 mm^3	0.550 x 0.080 x 0.037 mm^3	0.540 x 0.110 x 0.032 mm^3
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
CCDC	2281590	2331012	2331015

Table S4. Crystal structure data of $H_2TPP(p\text{-}CH_3O\text{-}Ph)_2$, $ZnTPP(m\text{-}CH_3O\text{-}Ph)_2$ & $CuTPP(m\text{-}CH_3O\text{-}Ph)_2$.

Table S5. Selected bond lengths (Å) and bond angles (°) of $H_2TPP(p\text{-}CH_3O\text{-}Ph)_2$, $ZnTPP(m\text{-}CH_3O\text{-}Ph)_2$ & $CuTPP(m\text{-}CH_3O\text{-}Ph)_2$.
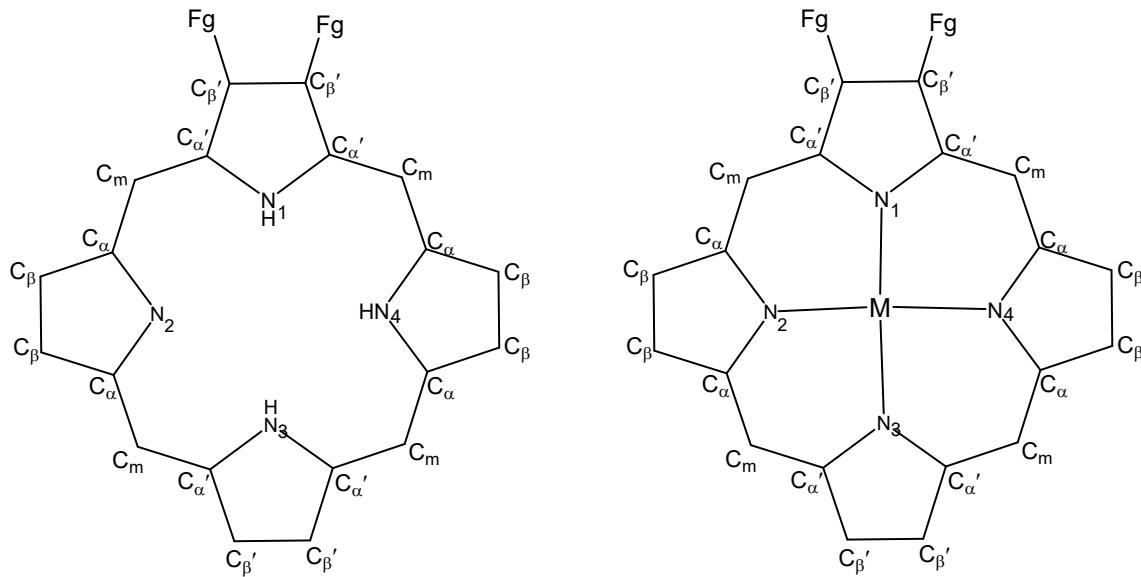
Bond Length (Å)

	$H_2TPP(p\text{-}CH_3O\text{-}Ph)_2$	$ZnTPP(m\text{-}CH_3O\text{-}Ph)_2$	$CuTPP(m\text{-}CH_3O\text{-}Ph)_2$
M-N	-	2.065 (6)	1.987 (2)
M-N′	-	2.102 (6)	1.999 (2)
N-C_α	1.381 (4)	1.377 (7)	1.380 (4)
N′-$C_{\alpha'}$	1.371 (3)	1.375 (7)	1.379 (3)
C_α-C_β	1.445 (4)	1.446 (8)	1.435 (3)
$C_{\alpha'}$-$C_{\beta'}$	1.444 (4)	1.452 (7)	1.444 (2)
C_β-C_β	1.344 (5)	1.343 (5)	1.348 (3)
$C_{\beta'}$-$C_{\beta'}$	1.357 (4)	1.351 (8)	1.351 (3)
C_α-C_m	1.397 (5)	1.406 (6)	1.397 (3)
$C_{\alpha'}$-C_m	1.401 (4)	1.409 (5)	1.395 (2)
ΔC_β (Å)[a]	0.014	0.128	0.558
$\Delta 24$ (Å)[b]	0.021	0.098	0.286
ΔMetal (Å)	-	0.379	0.066

Bond Angle (deg)

M-N-C_α	-	125.77 (5)	126.29 (3)
M-N′-C_α	-	126.07 (6)	126.59 (4)
N-M-N	-	161.63 (10)	173.82 (7)
N′-M-N′	-	160.78 (12)	177.57 (9)
N-C_α-C_m	126.77 (4)	126.24 (6)	125.39 (2)
N′-$C_{\alpha'}$-C_m	126.30 (5)	125.37 (7)	124.63 (3)

N-C_α-C_β	109.65 (3)	109.32 (4)	109.78 (2)
N'-$C_{\alpha'}$-$C_{\beta'}$	106.62 (4)	108.92 (5)	109.67 (4)
C_β- C_α-C_m	123.45 (4)	124.37 (5)	124.66 (3)
$C_{\beta'}$- $C_{\alpha'}$-C_m	127.31 (5)	125.66 (4)	125.49 (3)
C_α-C_m-$C_{\alpha'}$	125.42 (6)	125.15 (6)	123.31 (2)
C_α-C_β-C_β	107.35 (4)	107.39 (7)	107.24 (2)
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	108.11 (4)	107.47 (4)	107.17 (3)
C_α-N-C_α	105.99 (5)	106.54 (6)	105.70 (4)
$C_{\alpha'}$-N- $C_{\alpha'}$	110.52 (5)	107.41 (6)	106.02 (4)

[a]ΔC_β refers to the mean plane displacement of the β-pyrrole carbons

[b]$\Delta 24$ refers to the mean plane deviation of 24-atom core

esd's for all given bond length and bond angles are ± 5%

Table S6. Selected bond lengths (Å), bond angles (º) and dipole moments for the B3LYP/6-31G optimized geometries of $H_2TPP(p$-CH_3O-$Ph)_2$, $H_2TPP(m$-CH_3O-$Ph)_2$ & $H_2TPP(m,p$-CH_3O-$Ph)_2$.
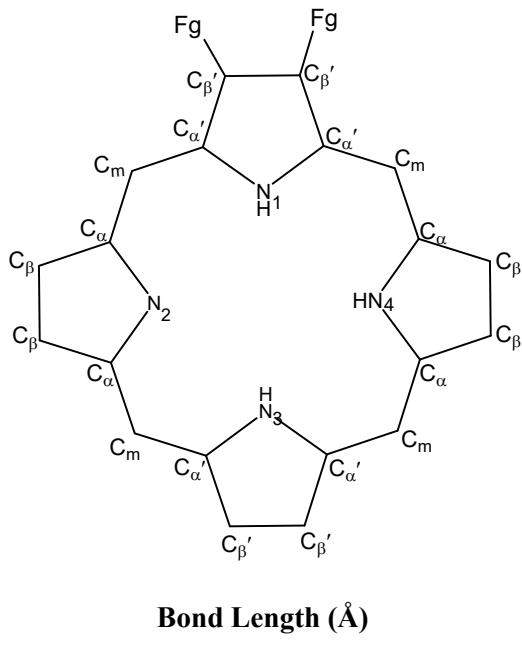
Bond Length (Å)

	$H_2TPP(p$-CH_3O-$Ph)_2$	$H_2TPP(m$-CH_3O-$Ph)_2$	$H_2TPP(m,p$-CH_3O-$Ph)_2$
N-C_α	1.366	1.365	1.367
N'-$C_{\alpha'}$	1.375	1.372	1.375
C_α-C_β	1.460	1.413	1.459
$C_{\alpha'}$-$C_{\beta'}$	1.439	1.408	1.439
C_β-C_β	1.353	1.352	1.351
$C_{\beta'}$-$C_{\beta'}$	1.380	1.379	1.380
C_α-C_m	1.413	1.460	1.416
$C_{\alpha'}$-C_m	1.409	1.439	1.412
ΔC_β (Å)[a]	0.430	0.480	0.490
$\Delta 24$ (Å)[b]	0.220	0.232	0.241

Bond Angle (deg)

	H$_2$TPP(p-CH$_3$O-Ph)$_2$	H$_2$TPP(m-CH$_3$O-Ph)$_2$	H$_2$TPP(m,p-CH$_3$O-Ph)$_2$
N-C$_\alpha$-C$_m$	126.15	126.23	126.29
N′-C$_{\alpha'}$-C$_m$	125.31	125.41	125.25
N-C$_\alpha$-C$_\beta$	110.85	110.86	110.61
N′-C$_{\alpha'}$-C$_{\beta'}$	106.46	106.43	106.40
C$_\beta$- C$_\alpha$-C$_m$	122.95	122.87	122.80
C$_{\beta'}$- C$_{\alpha'}$-C$_m$	128.17	127.62	128.27
C$_\alpha$-C$_m$-C$_{\alpha'}$	124.80	124.82	124.85
C$_\alpha$-C$_\beta$-C$_\beta$	106.35	106.35	106.35
C$_{\alpha'}$-C$_{\beta'}$-C$_{\beta'}$	107.93	107.95	107.96
C$_\alpha$-C$_n$-C$_\alpha$	105.51	105.49	105.85
C$_{\alpha'}$-C$_n$-C$_{\alpha'}$	111.05	111.09	111.12
Dipole moment	2.3734 D	5.1528 D	2.7013 D

[a]ΔC$_\beta$ refers to the mean plane displacement of the β-pyrrole carbons

[b]Δ24 refers to the mean plane deviation of 24-atom core

esd's for all given bond length and bond angles are ± 5%

Table S7. Selected bond lengths (Å), bond angles (º) and dipole moment for the B3LYP/LANL2DZ optimized geometries of ZnTPP(p-CH$_3$O-Ph)$_2$, ZnTPP(m-CH$_3$O-Ph)$_2$ & ZnTPP(m,p-CH$_3$O-Ph)$_2$.
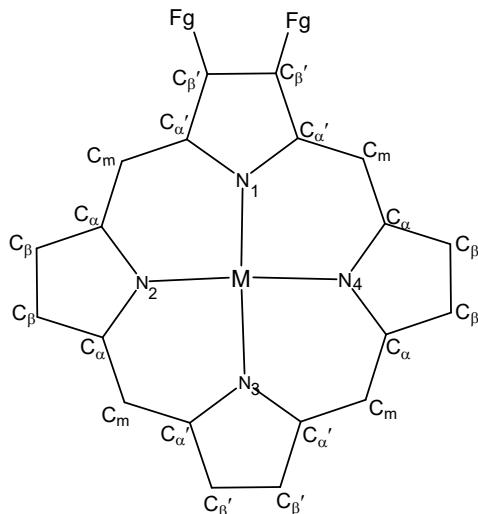
Bond Length (Å)

	ZnTPP(p-CH$_3$O-Ph)$_2$	ZnTPP(m-CH$_3$O-Ph)$_2$	ZnTPP(m,p-CH$_3$O-Ph)$_2$
M-N	2.058	2.055	2.053
M-N′	2.083	2.087	2.081
N-C$_\alpha$	1.375	1.376	1.378
N′-C$_{\alpha'}$	1.375	1.374	1.372
C$_\alpha$-C$_\beta$	1.446	1.447	1.449
C$_{\alpha'}$-C$_{\beta'}$	1.452	1.453	1.456
C$_\beta$-C$_\beta$	1.364	1.362	1.360
C$_{\beta'}$-C$_{\beta'}$	1.371	1.369	1.365
C$_\alpha$-C$_m$	1.412	1.412	1.412
C$_{\alpha'}$-C$_m$	1.414	1.416	1.416
ΔC$_\beta$ (Å)[a]	0.425	0.388	0.370
Δ24 (Å)[b]	0.203	0.186	0.177
ΔMetal (Å)	0.017	0.014	0.016

Bond Angle (deg)

|	ZnTPP(p-CH$_3$O-Ph)$_2$	ZnTPP(m-CH$_3$O-Ph)$_2$	ZnTPP(m,p-CH$_3$O-Ph)$_2$
M-N-C$_\alpha$	125.62	125.76	125.821
M-N′-C$_\alpha$	125.63	125.68	125.73
N-M-N	179.04	179.27	179.23
N′-M-N′	179.25	179.40	179.47
N-C$_\alpha$-C$_m$	126.05	126.17	126.21
N′-C$_{\alpha'}$-C$_m$	124.93	124.91	124.95
N-C$_\alpha$-C$_\beta$	109.06	109.07	109.53
N′-C$_{\alpha'}$-C$_{\beta'}$	109.25	109.19	109.19
C$_\beta$- C$_\alpha$-C$_m$	124.86	124.73	124.69
C$_{\beta'}$- C$_{\alpha'}$-C$_m$	125.80	125.86	125.83
C$_\alpha$-C$_m$-C$_{\alpha'}$	125.37	125.22	125.52
C$_\alpha$-C$_\beta$-C$_\beta$	107.20	107.24	107.28
C$_{\alpha'}$-C$_{\beta'}$-C$_{\beta'}$	106.92	106.94	106.87
C$_\alpha$-C$_n$-C$_\alpha$	107.41	107.43	107.42
C$_{\alpha'}$-C$_n$-C$_{\alpha'}$	107.52	107.57	107.58
Dipole moment	2.313 D	2.203 D	2.871 D

[a]ΔC$_\beta$ refers to the mean plane displacement of the β-pyrrole carbons

[b]Δ24 refers to the mean plane deviation of 24-atom core

esd's for all given bond length and bond angles are ± 5%
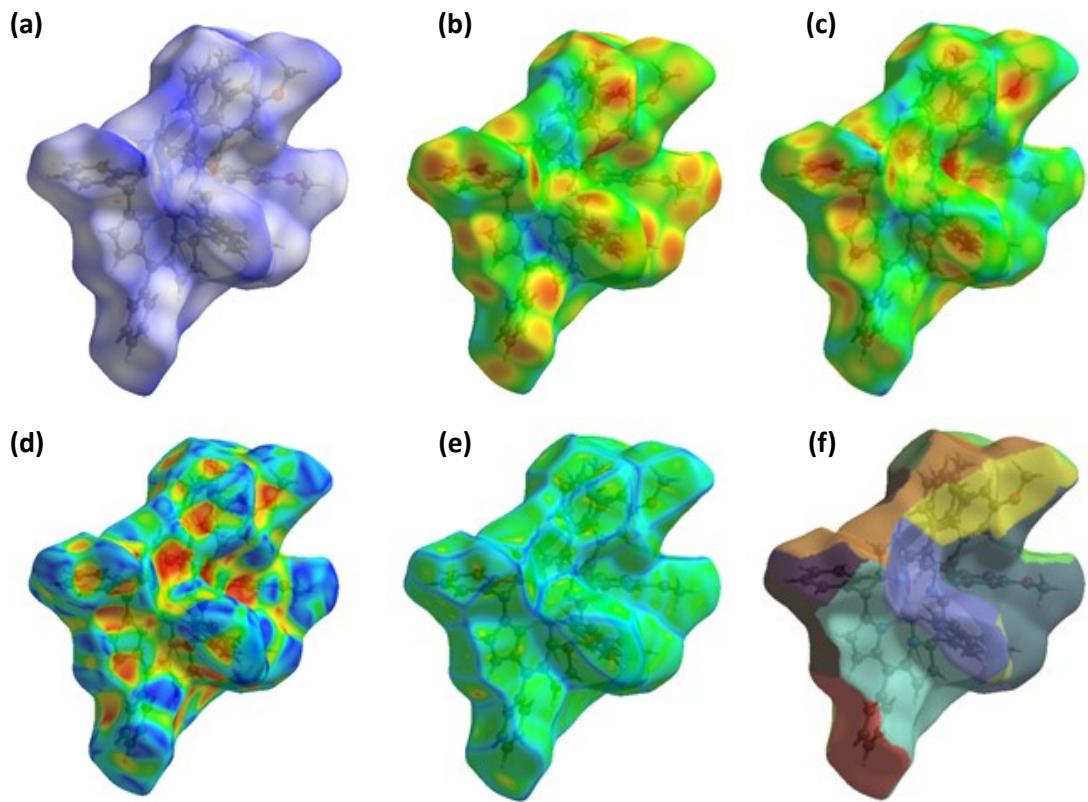
Figure S9. (a) Represent the dnorm plot, **(b)** represent the di plot, **(c)** represent the de plot, **(d)** represent the shape index **(e)** represent the curvedness plot and **(f)** represent the fragment patches with selected network of interaction of ZnTPP(*m*-CH₃O-Ph)₂.


Figure S10. 2D-fingerprint plots showing relative contribution of different types of interactions between atoms in crystal packing of ZnTPP(*m*-CH₃O-Ph)₂The di and de values are the closest

internal and external distances (in A˚) from given points on the Hirshfeld surface of ZnTPP(m-CH$_3$O-Ph)$_2$.

Figure S11. (a) Represent the dnorm plot, **(b)** represent the di plot, **(c)** represent the de plot, **(d)** represent the shape index **(e)** represent the curvedness plot and **(f)** represent the fragment patches with selected network of interaction of CuTPP(m-CH$_3$O-Ph)$_2$.

Figure S12. 2D-fingerprint plots showing relative contribution of different types of interactions between atoms in crystal packing of CuTPP(m-CH$_3$O-Ph)$_2$.The di and de values are the closest internal and external distances (in A˚) from given points on the hirshfeld surface of CuTPP(m-CH$_3$O-Ph)$_2$.

Figure S13. Optimized structures of synthesized molecules MTPP(p-CH$_3$O-Ph)$_2$, M = 2H, Zn (a, b), MTPP(m-CH$_3$O-Ph)$_2$, M = 2H, Zn (c, d) & MTPP(m,p-CH$_3$O-Ph)$_2$, M = 2H, Zn (e, f) respectively, by using B3LYP-6-31G (d, p) level of theory in combination with LANL2DZ basis set.

Figure S14. B3LYP/LanL2DZ optimized geometries showing top as well as side views of ZnTPP(*p*-CH₃O-Ph)₂ (a & b), ZnTPP(*m*-CH₃O-Ph)₂ (c & d) and ZnTPP(*m,p*-CH₃O-Ph)₂ (e & f).


(a) **(c)** **(e)**

(b) **(d)** **(f)**

Figure S15. B3LYP/6-31G optimized geometries showing direction of dipole moment of MTPP(*p*-CH₃O-Ph)₂, M = 2H, Zn (a, b), MTPP(*m*-CH₃O-Ph)₂, M = 2H, Zn (c, d) & MTPP(*m,p*-CH₃O-Ph)₂, M = 2H, Zn (e, f) respectively. by using B3LYP-6-31G (d, p) level of theory in combination with LANL2DZ basis set Color codes for atoms: C (black), N (blue), H (white) and O (red) and Zn (light blue).



LUMO **LUMO +1** **LUMO +2**

HOMO **HOMO -1** **HOMO -2**

Figure S16. B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of H$_2$TPP(p-CH$_3$O-Ph)$_2$ respectively (having isosurface contour value of 0.03).

LUMO

LUMO +1

LUMO +2

HOMO

HOMO -1

HOMO -2

Figure S17. B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of ZnTPP(p-CH$_3$O-Ph)$_2$ respectively (having isosurface contour value of 0.03).

LUMO

LUMO +1

LUMO +2

HOMO

HOMO -1

HOMO -2

Figure S18. B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of H$_2$TPP(m-CH$_3$O-Ph)$_2$ respectively (having isosurface contour value of 0.03).

**Figure S19.** B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of H$_2$TPP(m-CH$_3$O-Ph)$_2$ respectively (having isosurface contour value of 0.03).

Figure S20. B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of $H_2TPP(m,p\text{-}CH_3O\text{-}Ph)_2$ respectively (having isosurface contour value of 0.03).

LUMO   LUMO +1   LUMO +2

HOMO   HOMO -1   HOMO -2

Figure S21. B3LYP/6-31G optimized geometries showing Frontier Molecular Orbitals (FMOs) of $ZnTPP(m,p\text{-}CH_3O\text{-}Ph)_2$ respectively (having isosurface contour value of 0.03).

(a)   (b)   (c)

Figure S22. Molecular electrostatic potential (MEP) Zinc porphyrins:(a) $ZnTPP(p\text{-}CH_3O\text{-}Ph)_2$ (b) $ZnTPP(m\text{-}CH_3O\text{-}Ph)_2$ and (c) $ZnTPP(m,p\text{-}CH_3O\text{-}Ph)_2$ using the B3LYP/ 6 31G (d, p) technique in the Gaussian 16W, in gas phase.

Table S8. The calculated Absorption, Oscillator strength, Molecular Transitions (M.T.), % weight contribution (% Ci > 10) of synthesized [ZnTPP(R)$_2$ R = p-CH$_3$O-Ph, m-CH$_3$O-Ph & m,p- CH$_3$O-Ph] at B3LYP-6-31G (d, p) level of theory in combination with LANL2DZ basis set.

Compounds	State	Molecular transitions (M.T)	Excited state energy (eV)	Weight contribution (%Ci)	Calculated λ (nm) in DCM	Oscillatory strength (f)	Experimental λ (nm) in DCM
ZnTPP(p-CH$_3$O-Ph)$_2$	S1	H-1 → L +1	2.1826 eV	30	568	0.0753	589
		H → L		69			
	S2	H-1 → L	2.2076 eV	37	562	0.0261	553
		H → L +1		62			
	S3	H-2 → L	2.7977 eV	79	443	0.1741	486
	S4	H-3 → L	2.9252 eV	89	424	0.0382	425
	S5	H-3 → L +1	2.9348 eV	61	422	0.4469	
		H-2 → L		14			
		H-2 → L+1		10			
ZnTPP(m-CH$_3$O-Ph)$_2$	S1	H-1 → L +1	2.1963eV	31	565	0.0658	594
		H → L		68			
	S2	H-1 → L	2.2196 eV	39	559	0.0192	552
		H → L +1		61			
	S3	H-2 → L	2.7832 eV	97	446	0.004	487
	S4	H-3 → L	2.9038 eV	19	427	0.021	
		H-2 → L+1		79			423
	S5	H-3 → L	2.9227 eV	51	424	0.4361	
		H-2 → L+1		18			
		H-1 → L		16			
ZnTPP(m,p-CH$_3$O-Ph)$_2$	S1	H-1 → L +1	2.2021 eV	32	563	0.0605	592
		H → L		68			
	S2	H-1 → L	2.236 eV	39	558	0.0168	551
		H → L +1		60			
	S3	H-2 → L	2.8053 eV	85	442	0.1536	486
	S4	H-2 → L+1		77		0.1641	
	S5	H-3 → L	2.9384 eV	89	419	0.0138	422

Figure S23. ^{1}H NMR spectrum of H$_2$TPP(p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
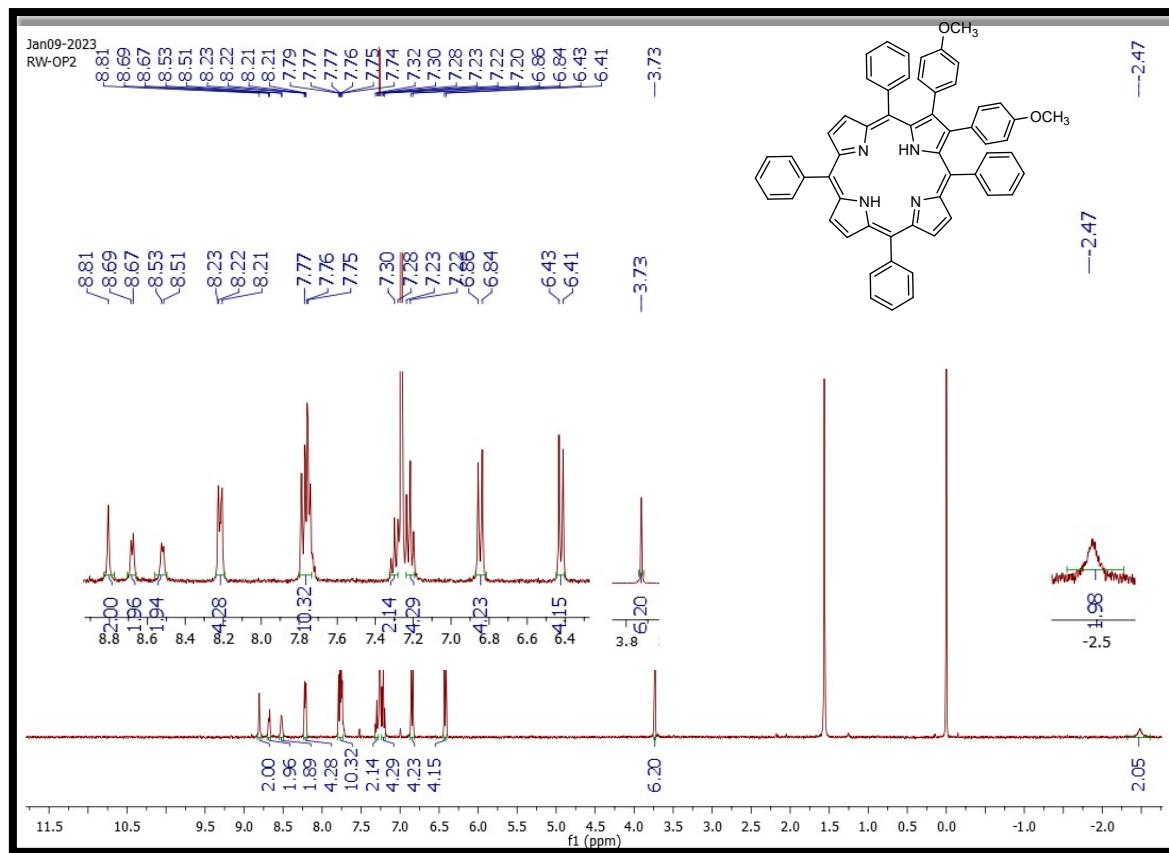
Figure S24. ^{1}H NMR spectrum of ZnTPP(p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
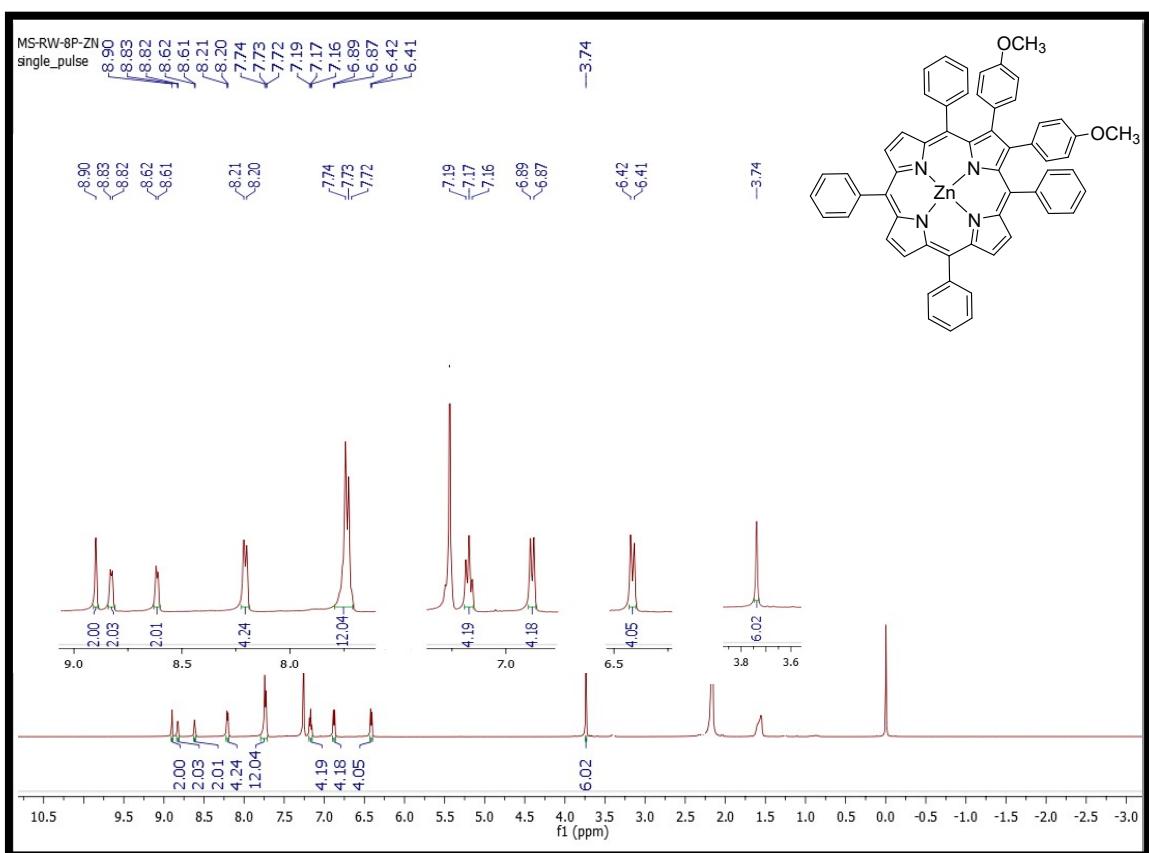
Figure S25. ^{1}H NMR spectrum of NiTPP(p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
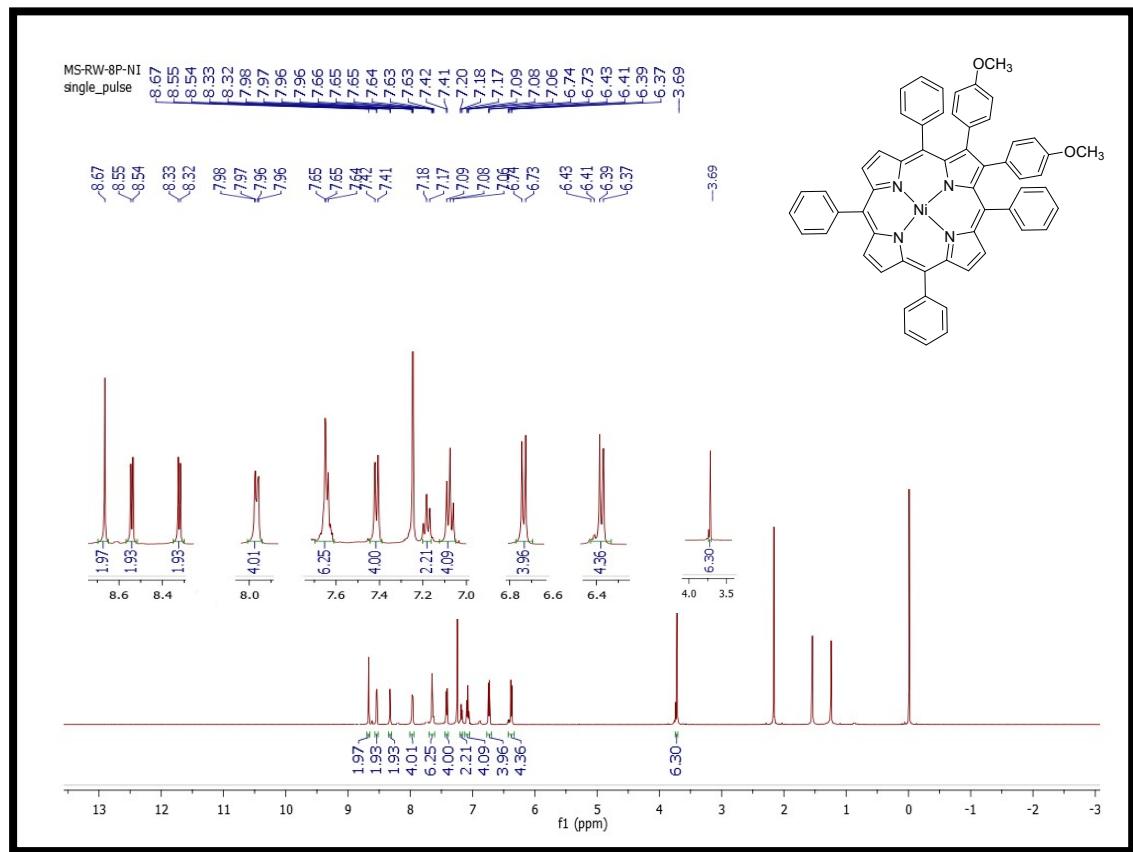
Figure S26. ^{1}H NMR spectrum of H$_2$TPP(m-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
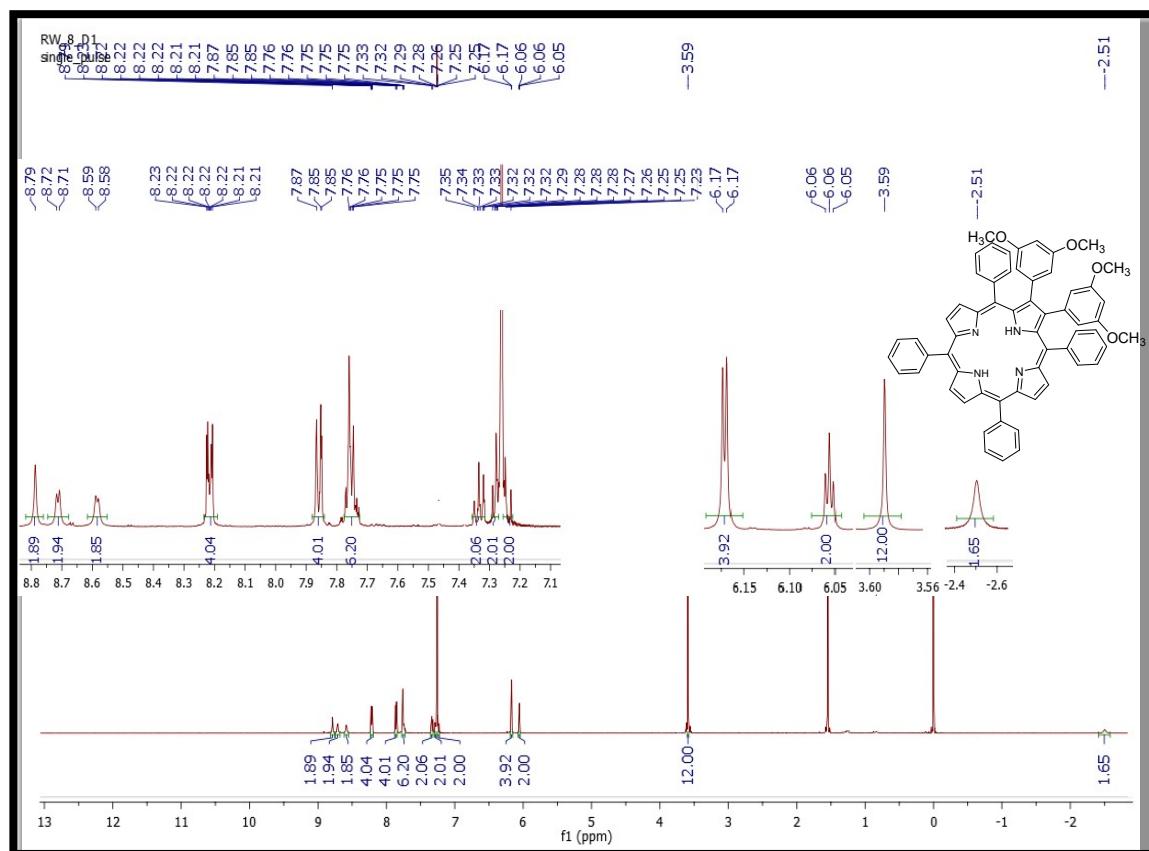
Figure S27. ^{1}H NMR spectrum of ZnTPP(m-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.

Figure S28. ^{1}H NMR spectrum of NiTPP(m-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
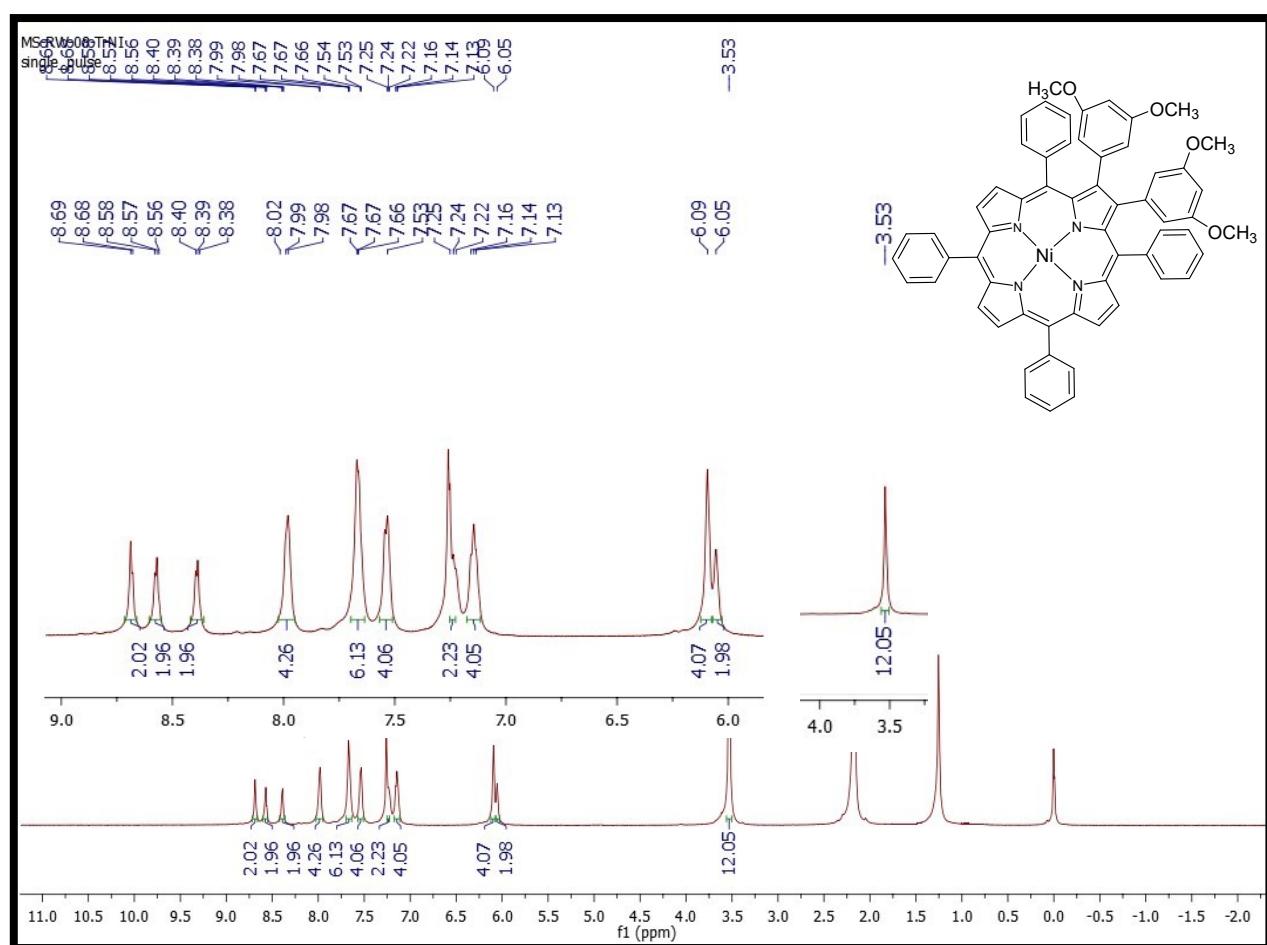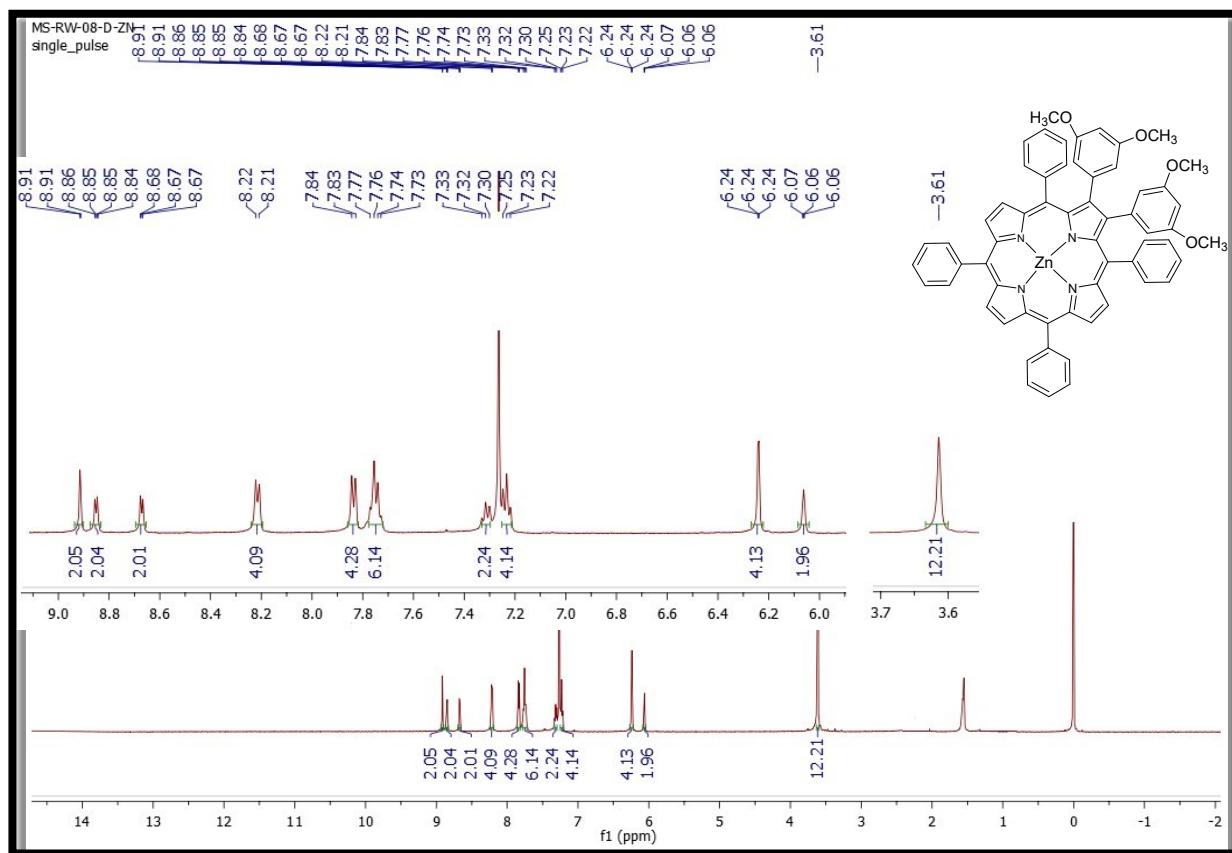
Figure S29. ^{1}H NMR spectrum of H$_2$TPP(m,p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
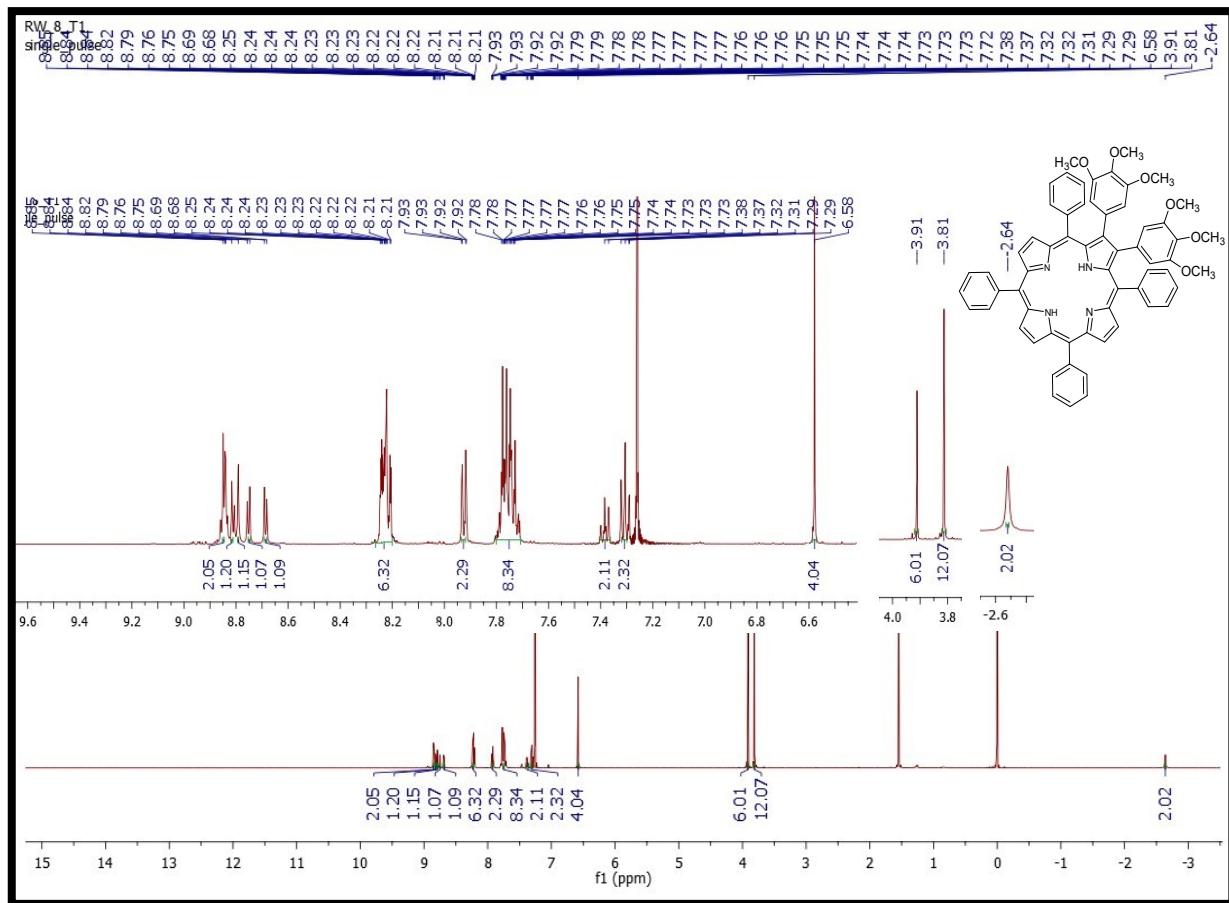
Figure S30. ^{1}H NMR spectrum of ZnTPP(m,p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
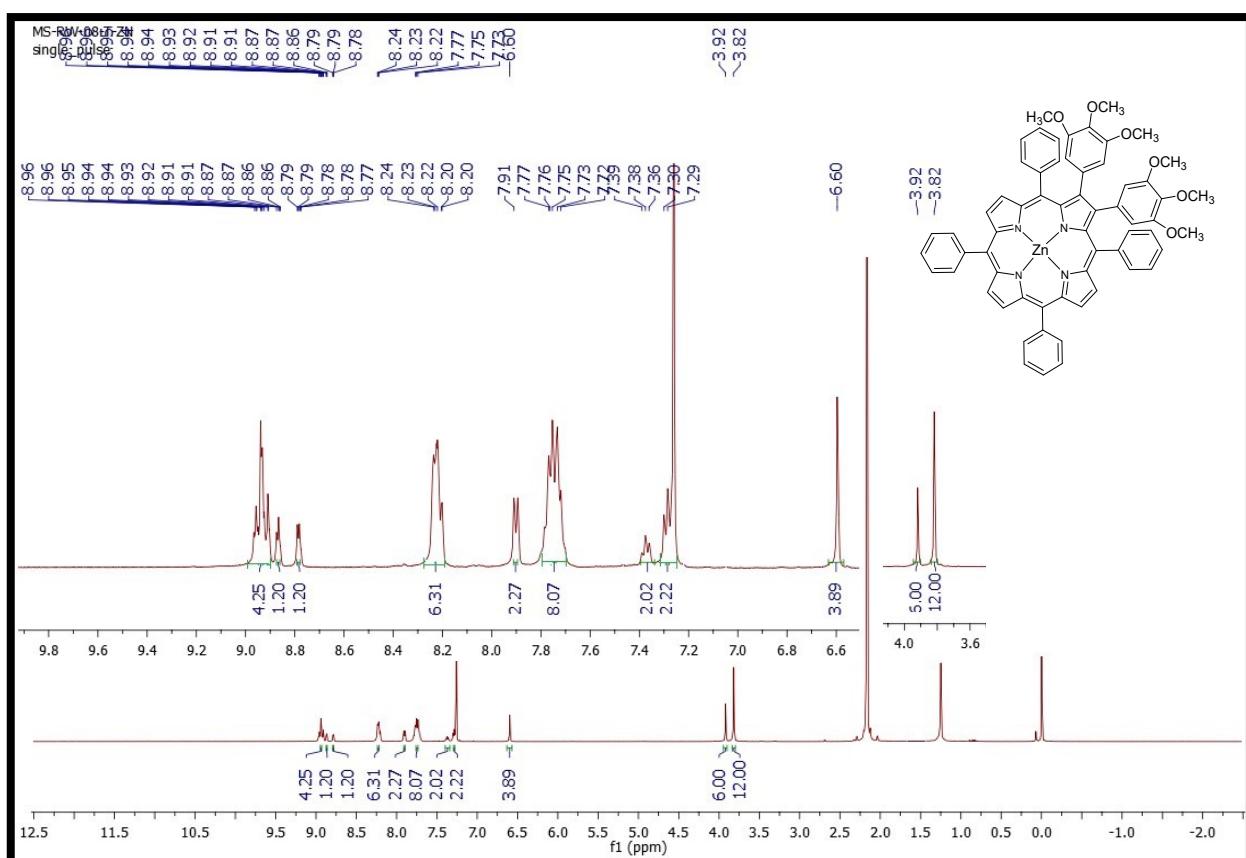
Figure S31. ^{1}H NMR spectrum of NiTPP(m,p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
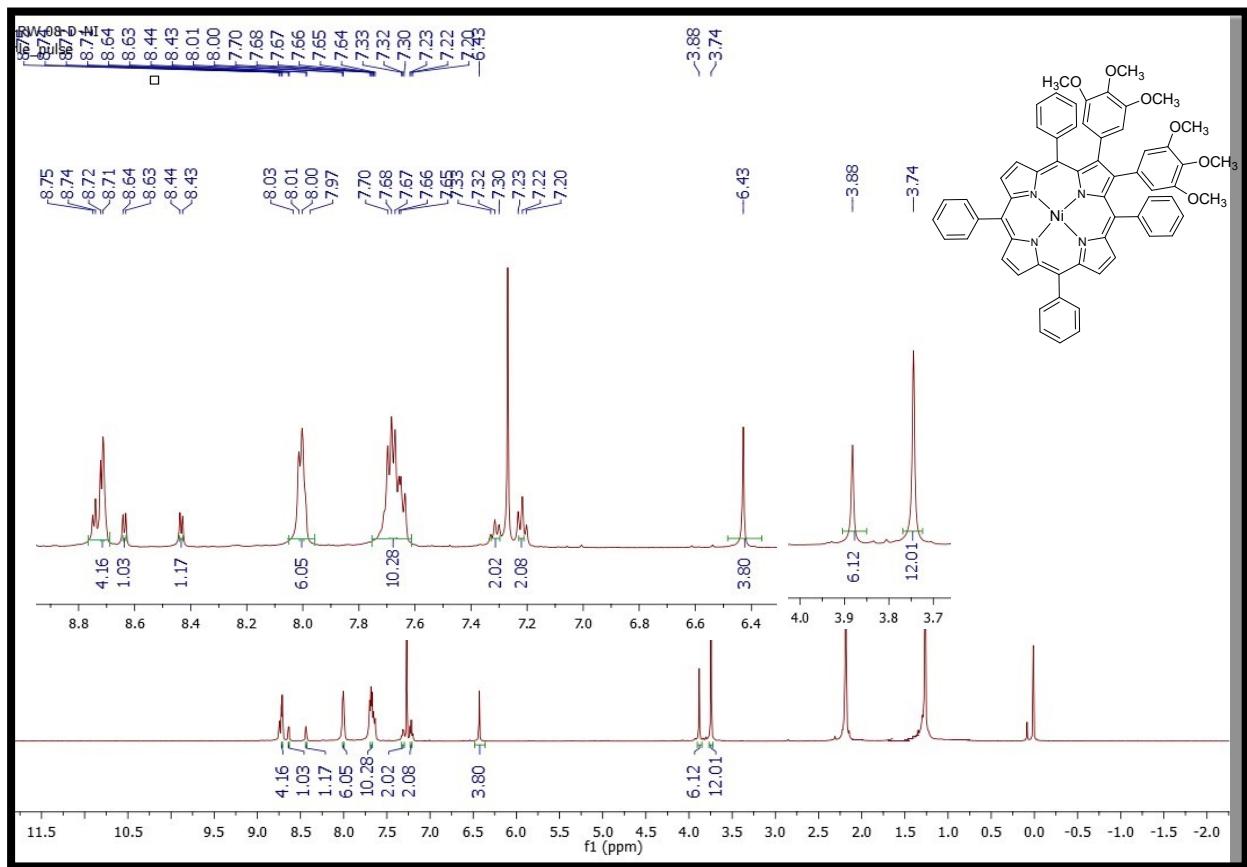
Figure S32. ^{13}C NMR spectrum of H$_2$TPP(p-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
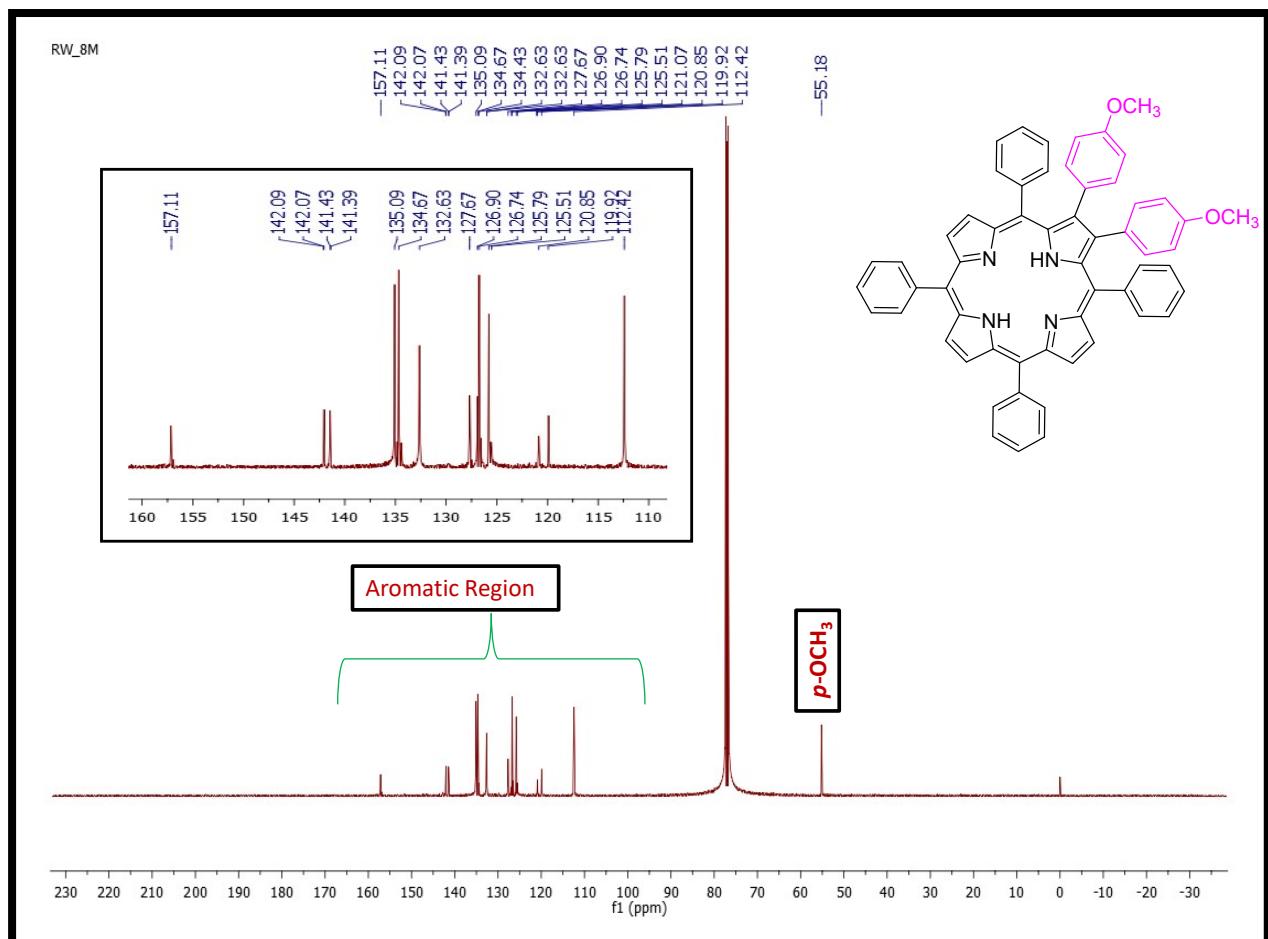
Figure S33. ^{13}C NMR spectrum of H$_2$TPP(*m*-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
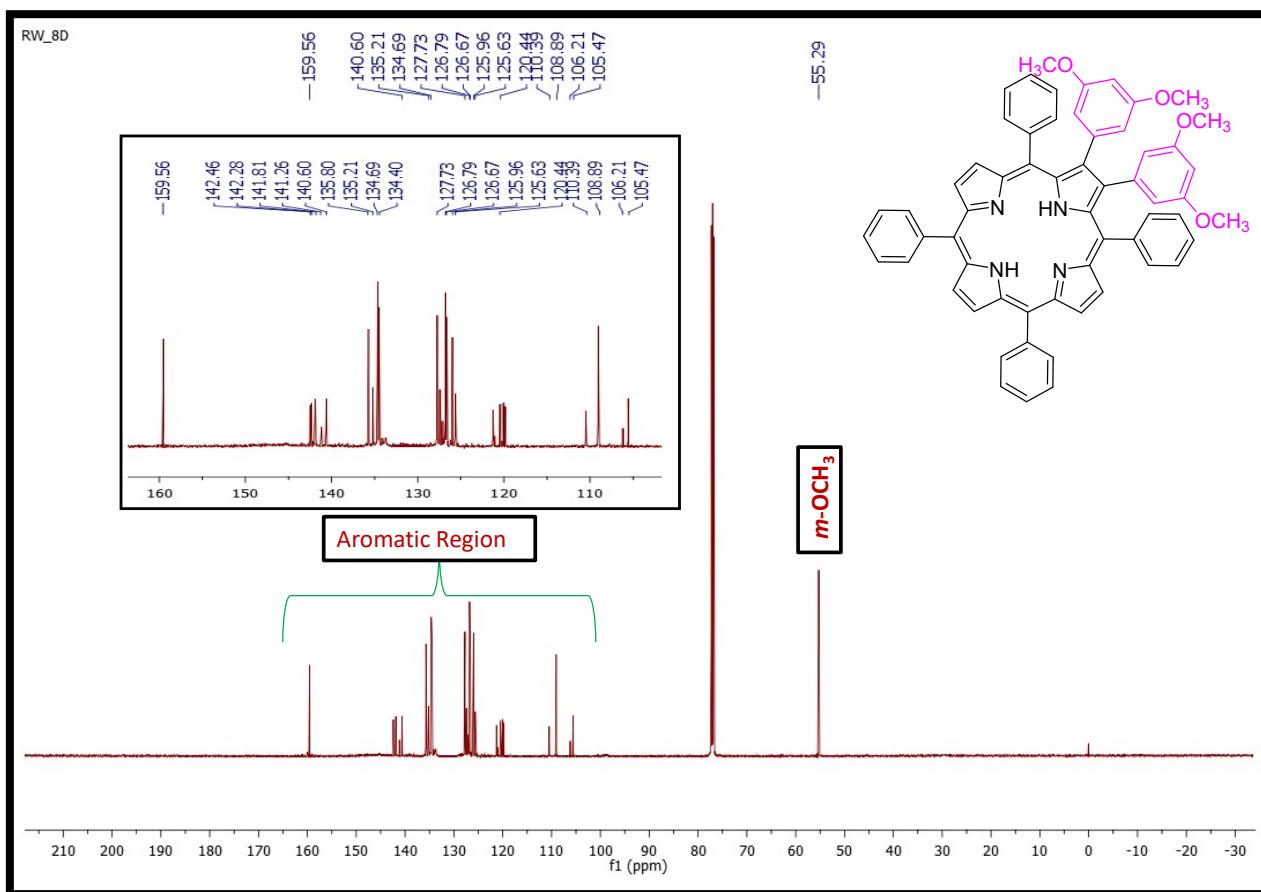
Figure S34. ^{13}C NMR spectrum of H$_2$TPP(*m,p*-CH$_3$O-Ph)$_2$ in CDCl$_3$ at 298 K.
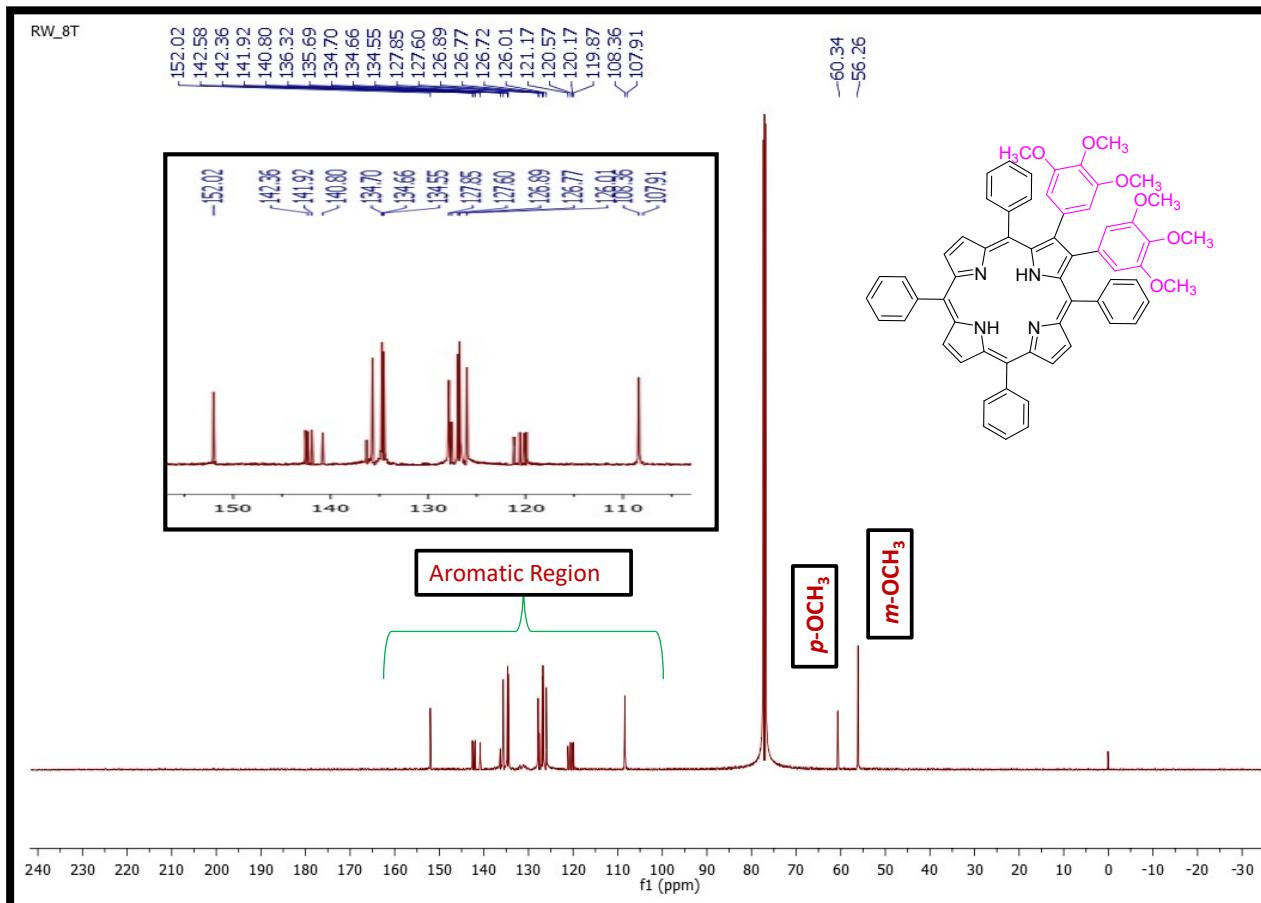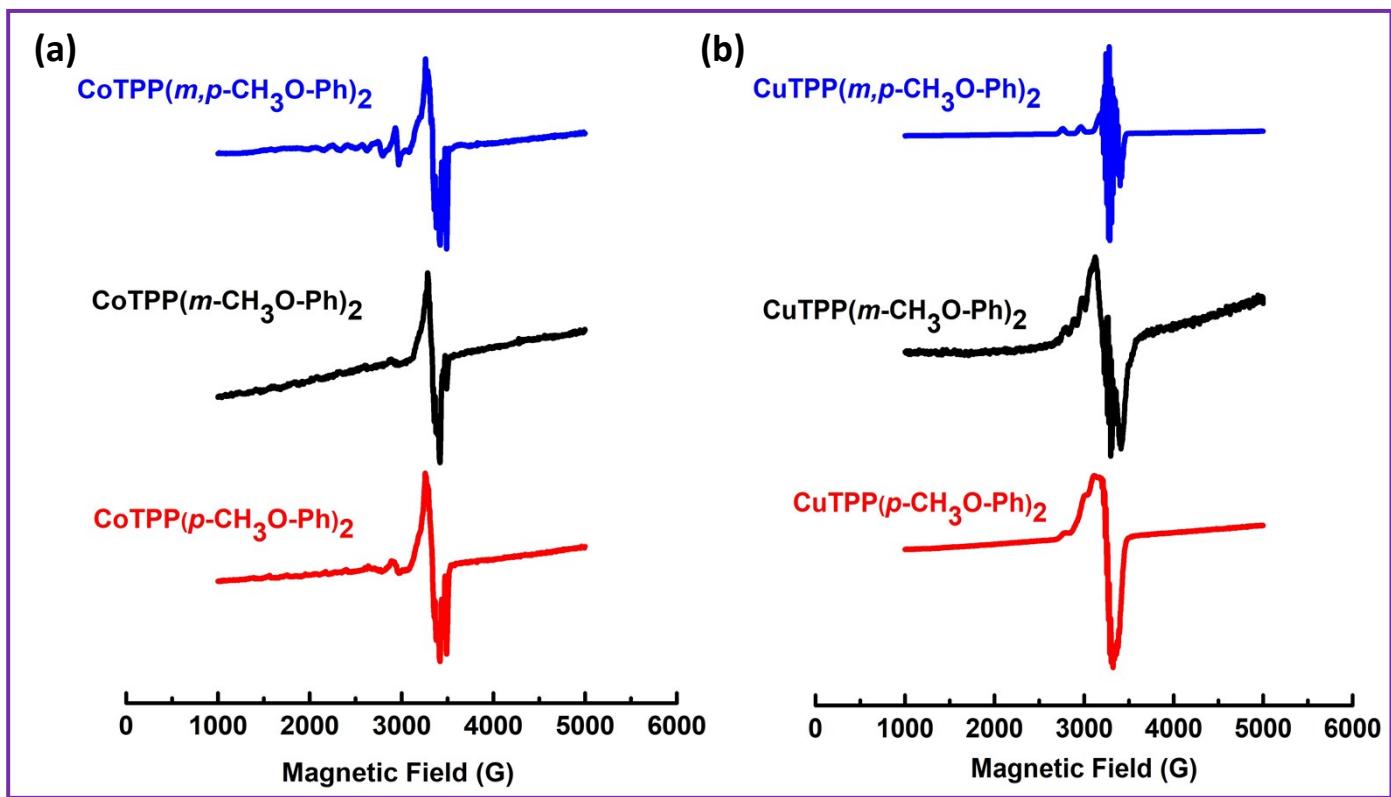
Figure S35. X-band EPR Spectra of (a) CoTPP(R)$_2$, where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph (b) CuTPP(R)$_2$; where R = *p*-CH$_3$O-Ph, *m*-CH$_3$O-Ph & *m,p*-CH$_3$O-Ph in toluene at 100 K, with EPR parameters: microwave frequency 9.41 GHz, incident microwave power 1.7 mW, modulation frequency 100 kHz.

Figure S36. HRMS spectrum of H$_2$TPP(*p*-CH$_3$O-Ph)$_2$.
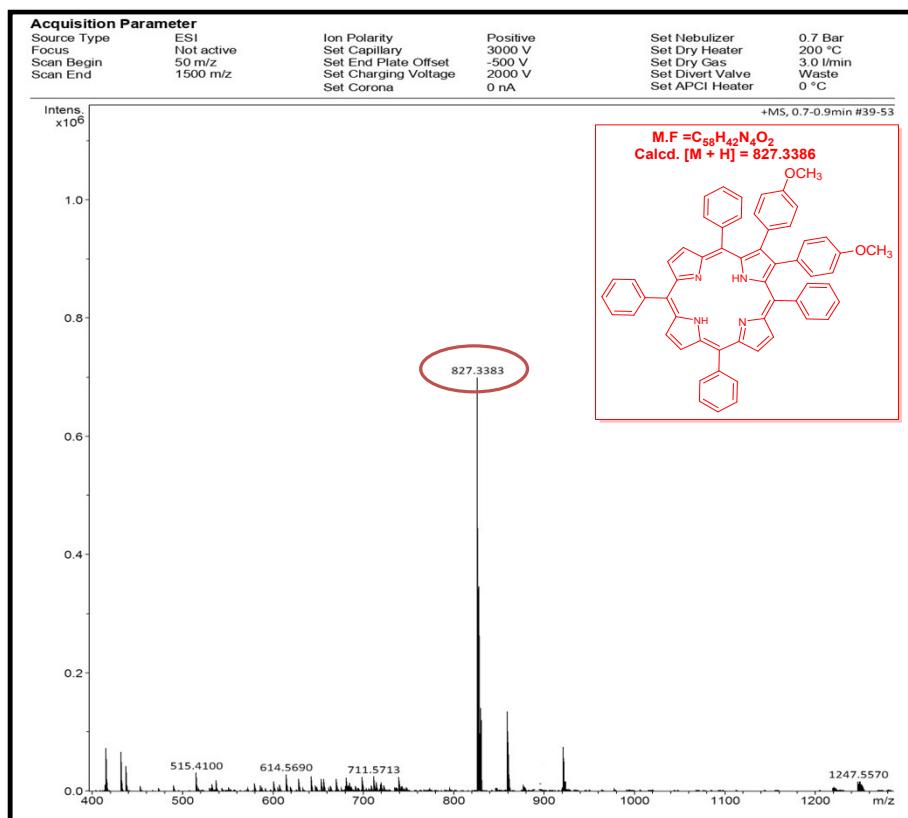
**Figure S37**. HRMS spectrum of ZnTPP(*p*-CH₃O-Ph)₂.
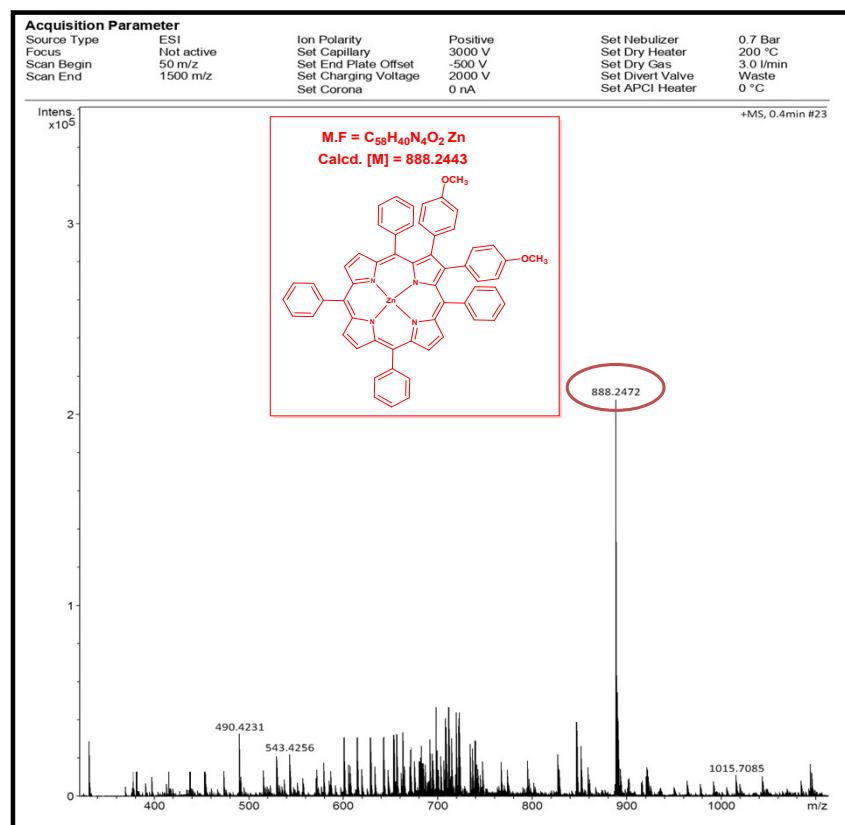
Figure S38. HRMS spectrum of NiTPP(*p*-CH₃O-Ph)₂.
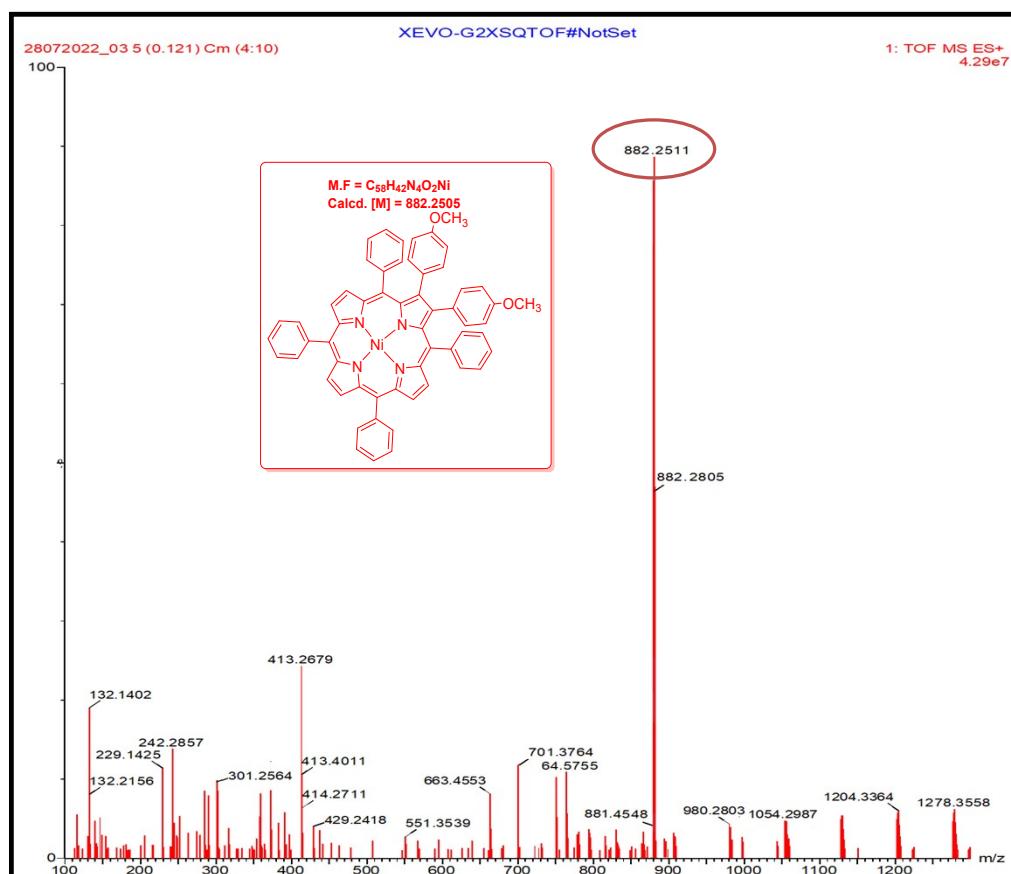
Figure S39. HRMS spectrum of CuTPP(*p*-CH₃O-Ph)₂.
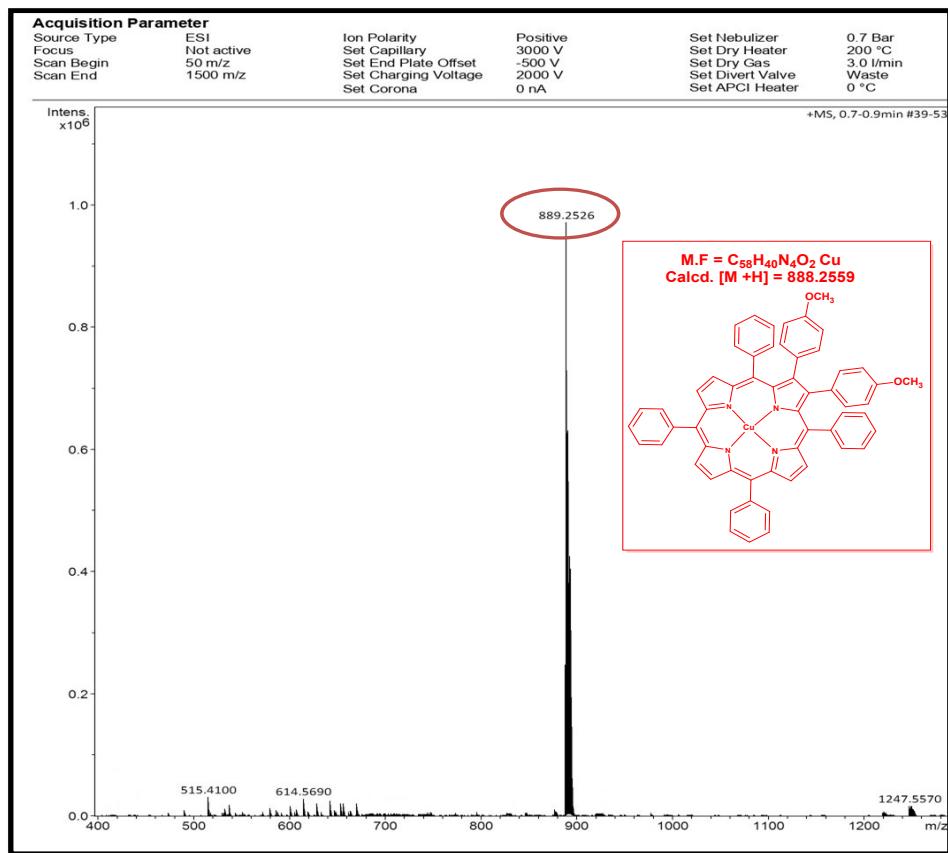

Figure S40. HRMS spectrum of CoTPP(*p*-CH₃O-Ph)₂.
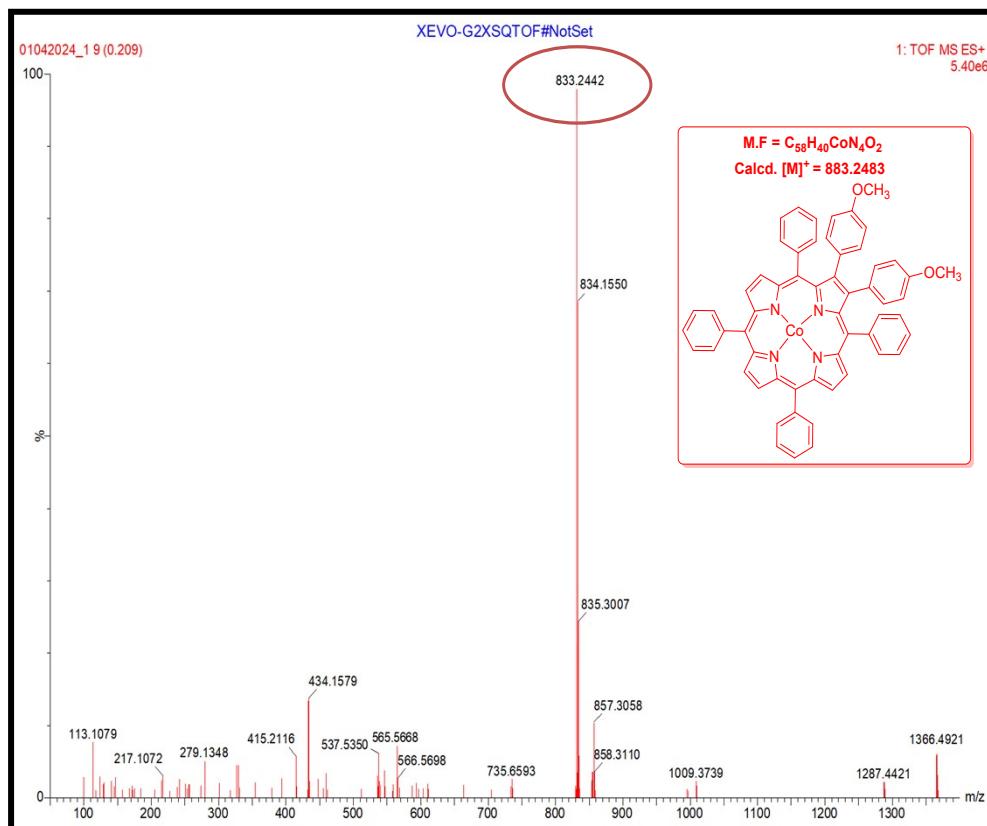
Figure S41. HRMS spectrum of H$_2$TPP(m-CH$_3$O-Ph)$_2$.
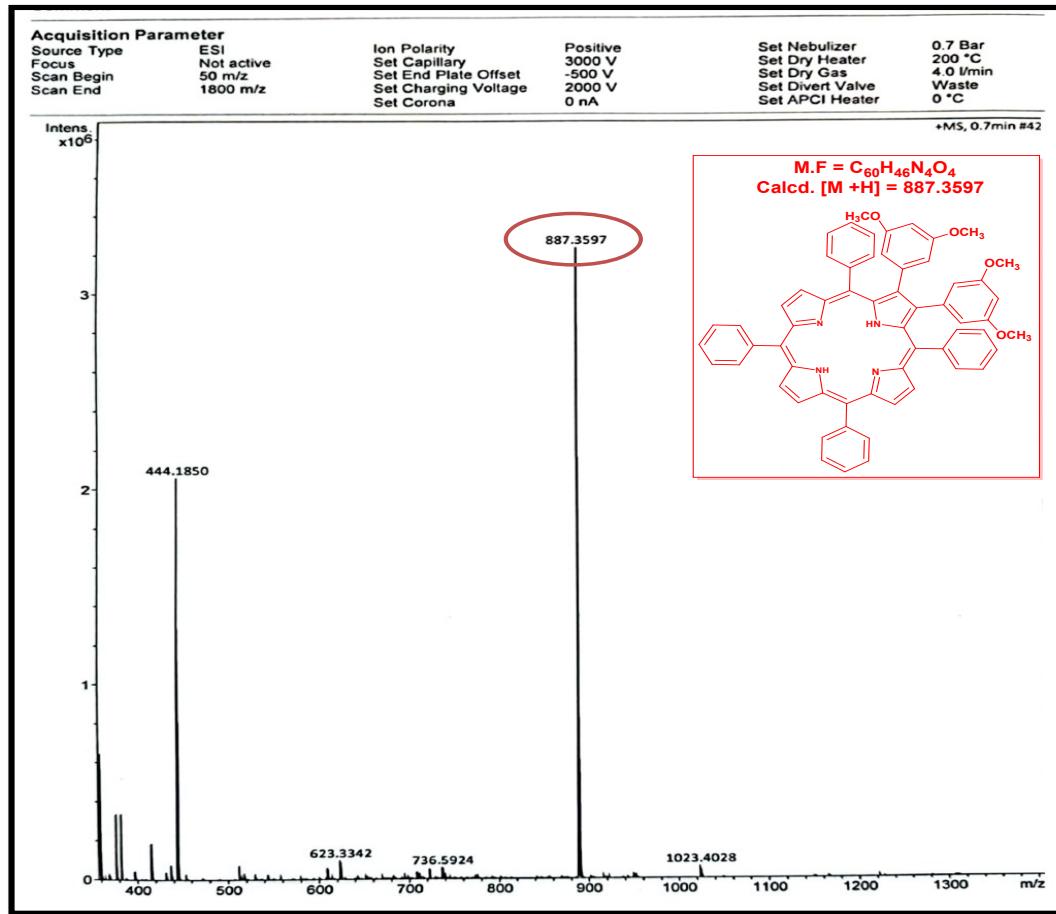
Figure S42. HRMS spectrum of ZnTPP(m-CH$_3$O-Ph)$_2$.
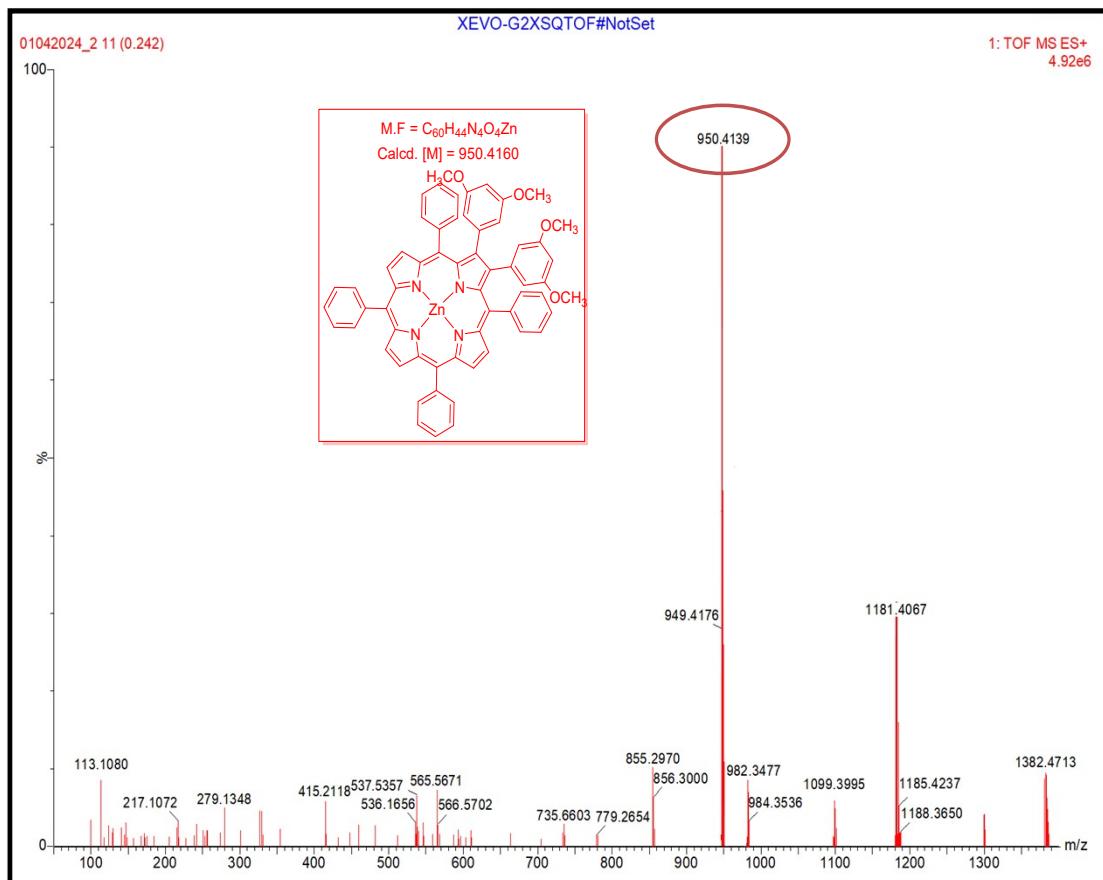
Figure S43. HRMS spectrum of NiTPP(*m*-CH$_3$O-Ph)$_2$.
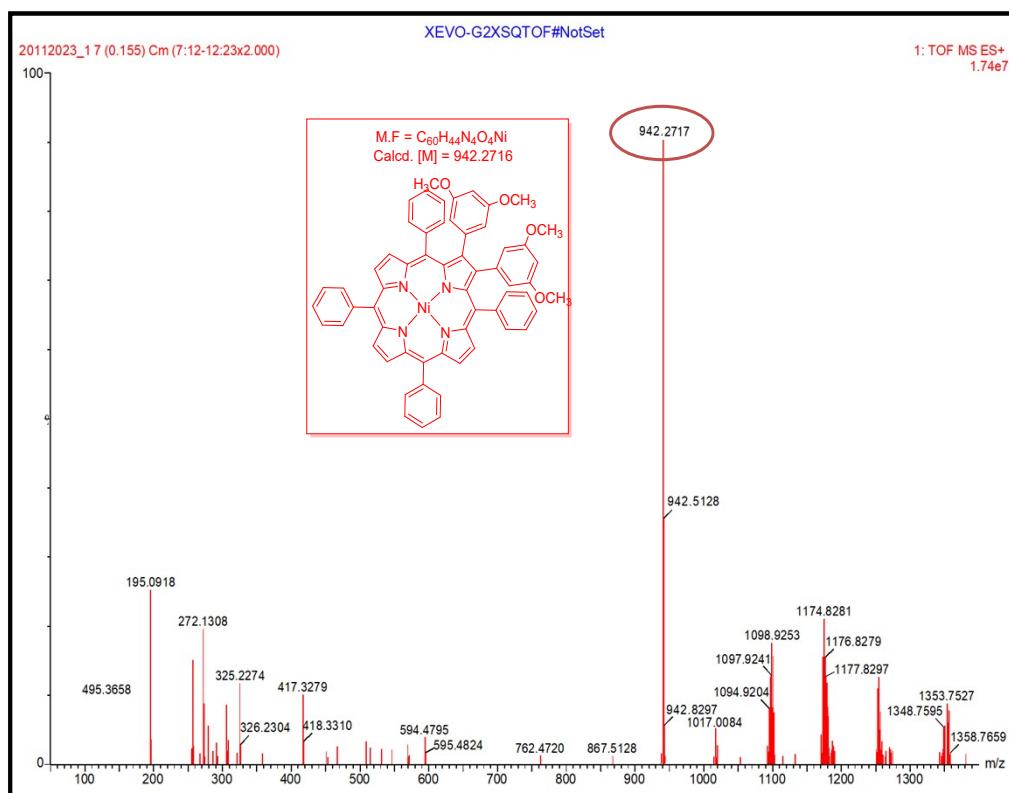
Figure S44. HRMS spectrum of CuTPP(*m*-CH$_3$O-Ph)$_2$.
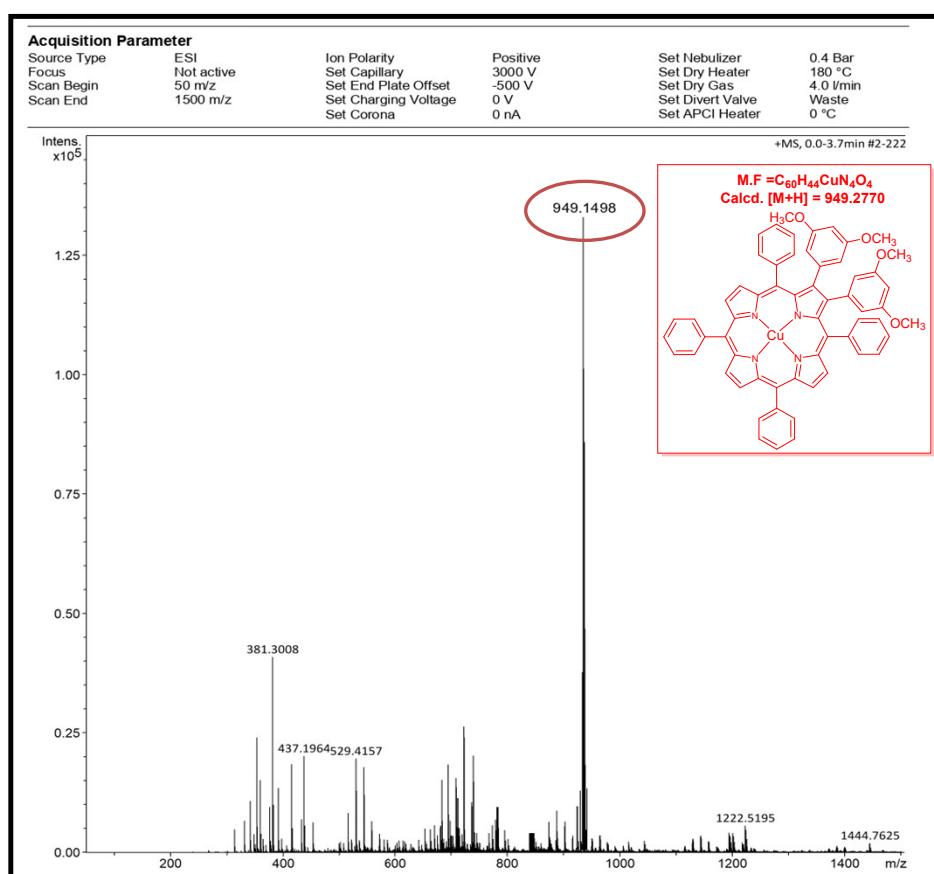
Figure S45. HRMS spectrum of CoTPP(*m*-CH₃O-Ph)₂.
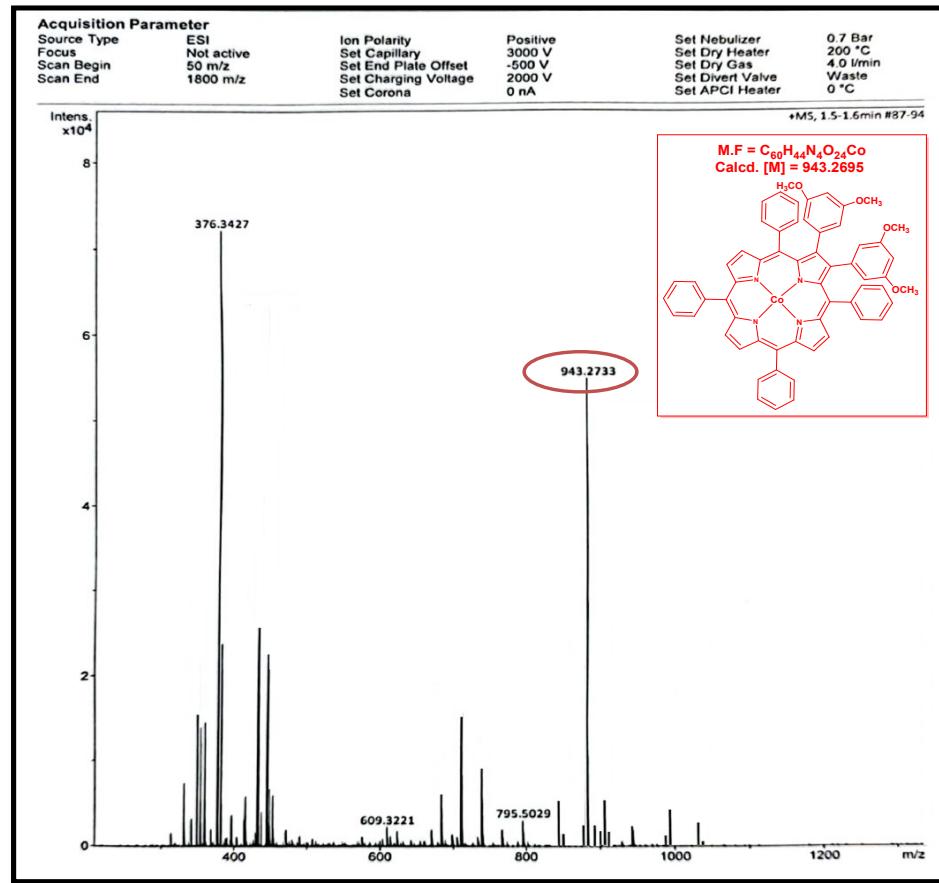
**Figure S46**. HRMS spectrum of H₂TPP(*m,p*-CH₃O-Ph)₂.
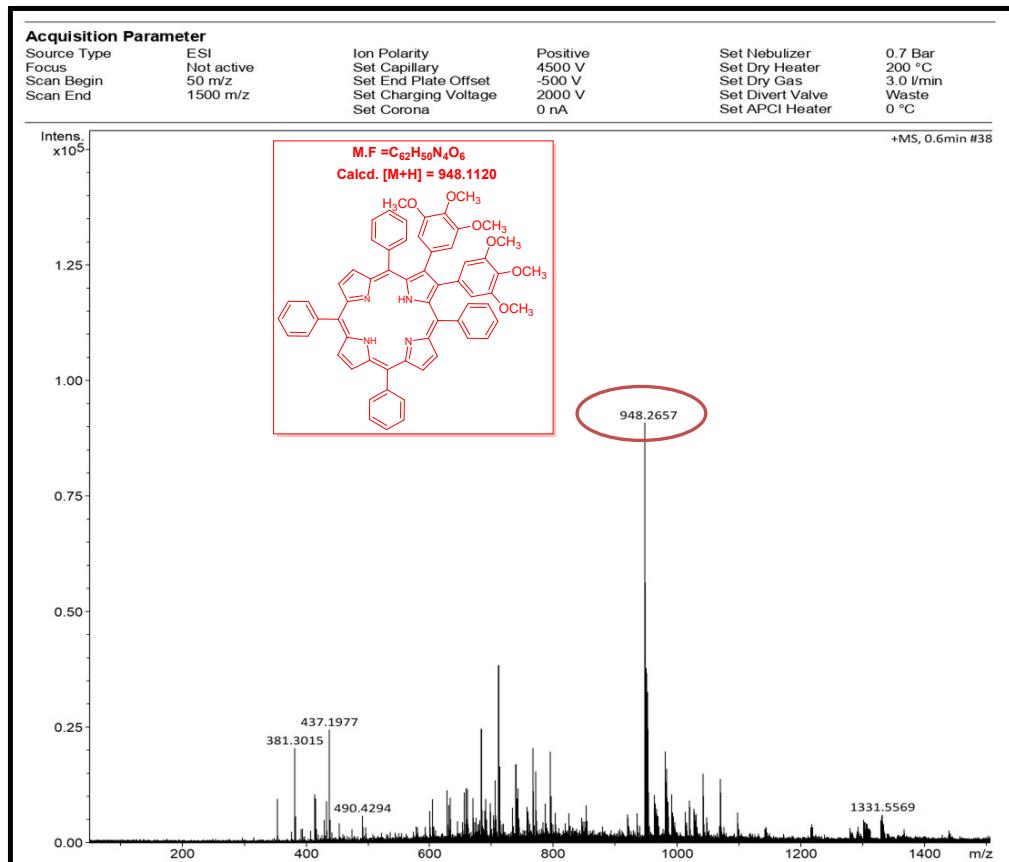
Figure S47. HRMS spectrum of ZnTPP(*m,p*-CH₃O-Ph)₂.
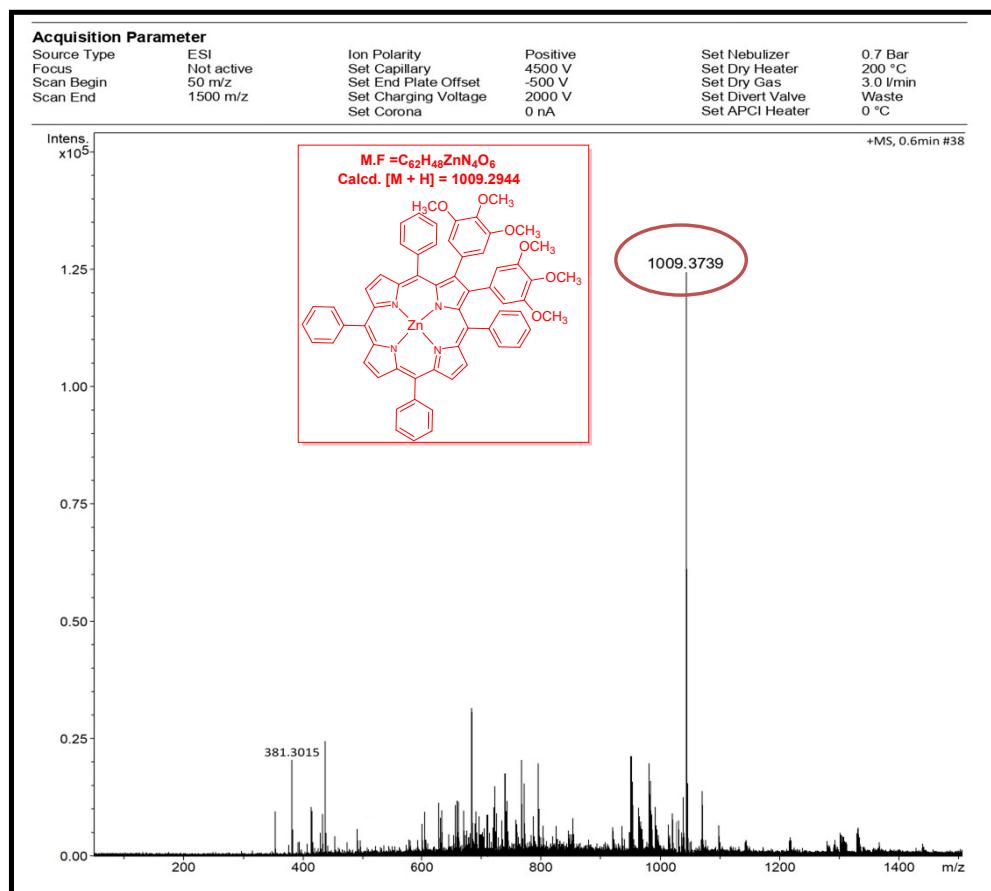
**Figure S48**. HRMS spectrum of NiTPP(*m,p*-CH₃O-Ph)₂.
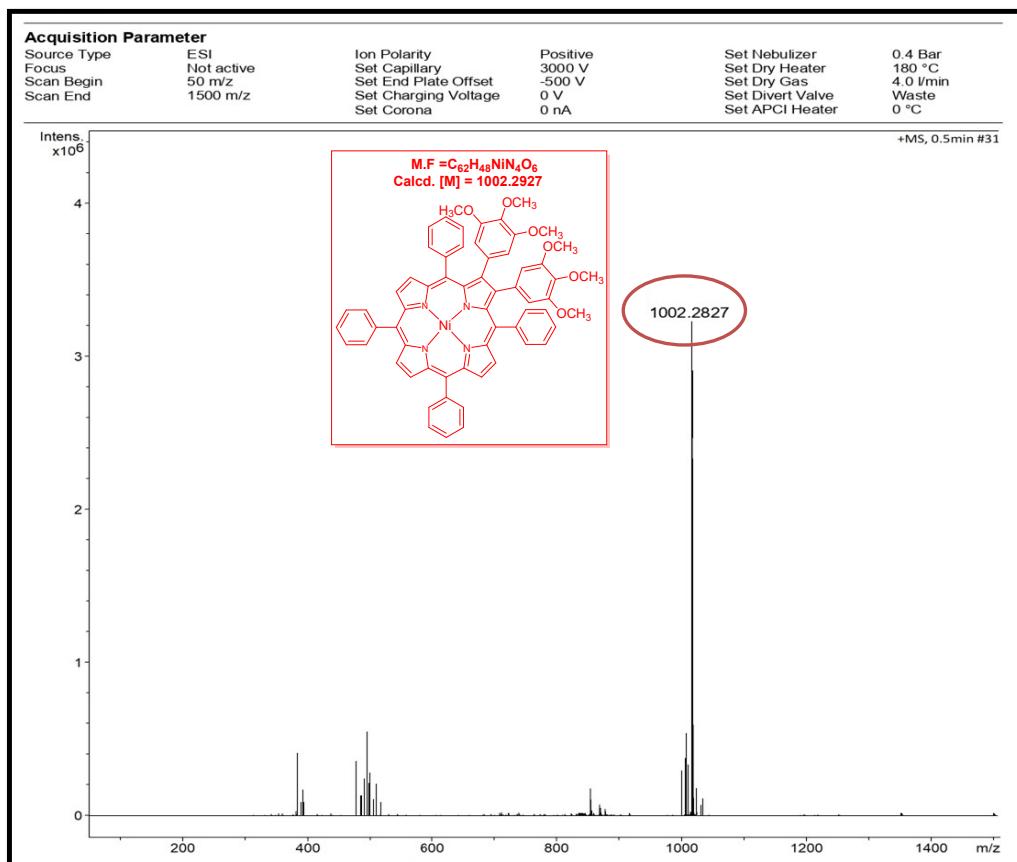
Figure S49. HRMS spectrum of CoTPP(*m,p*-CH$_3$O-Ph)$_2$.
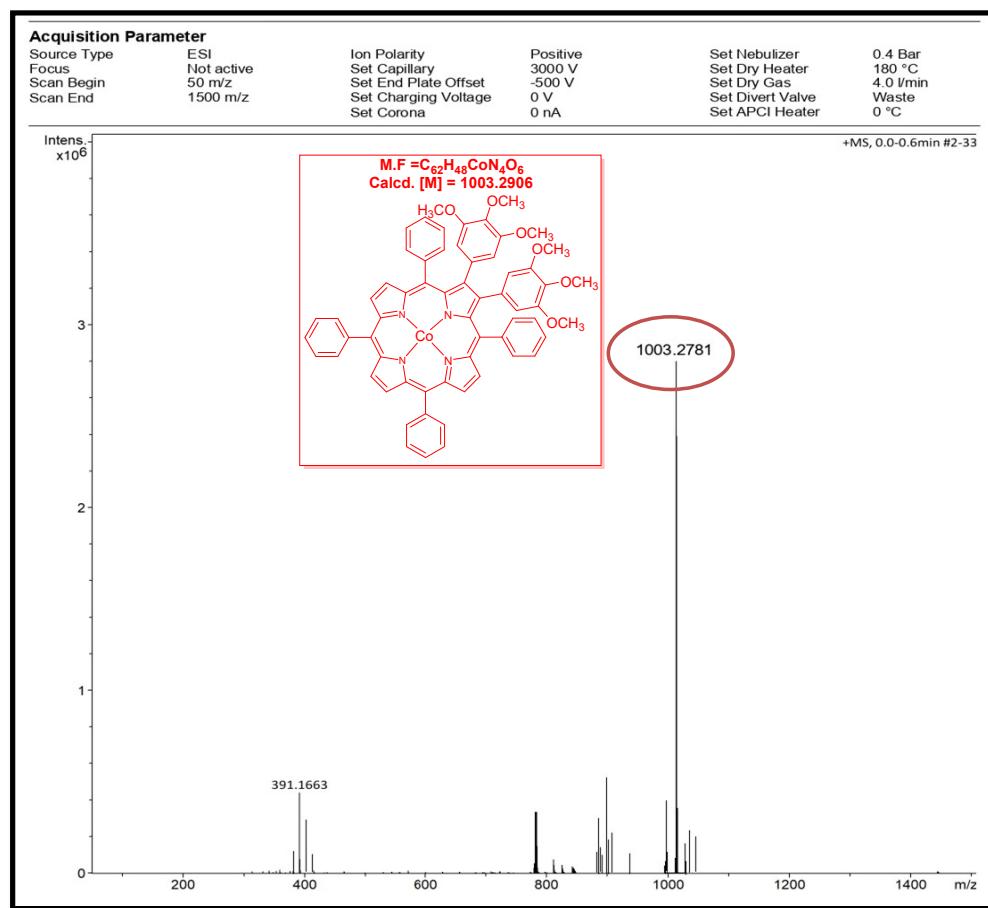
Figure S50. HRMS spectrum of CuTPP(*m,p*-CH$_3$O-Ph)$_2$.