Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information for

Mono- and Tri-*β*-Substituted Unsymmetrical Metalloporphyrins: Synthesis, Structural, Spectral and Electrochemical Properties

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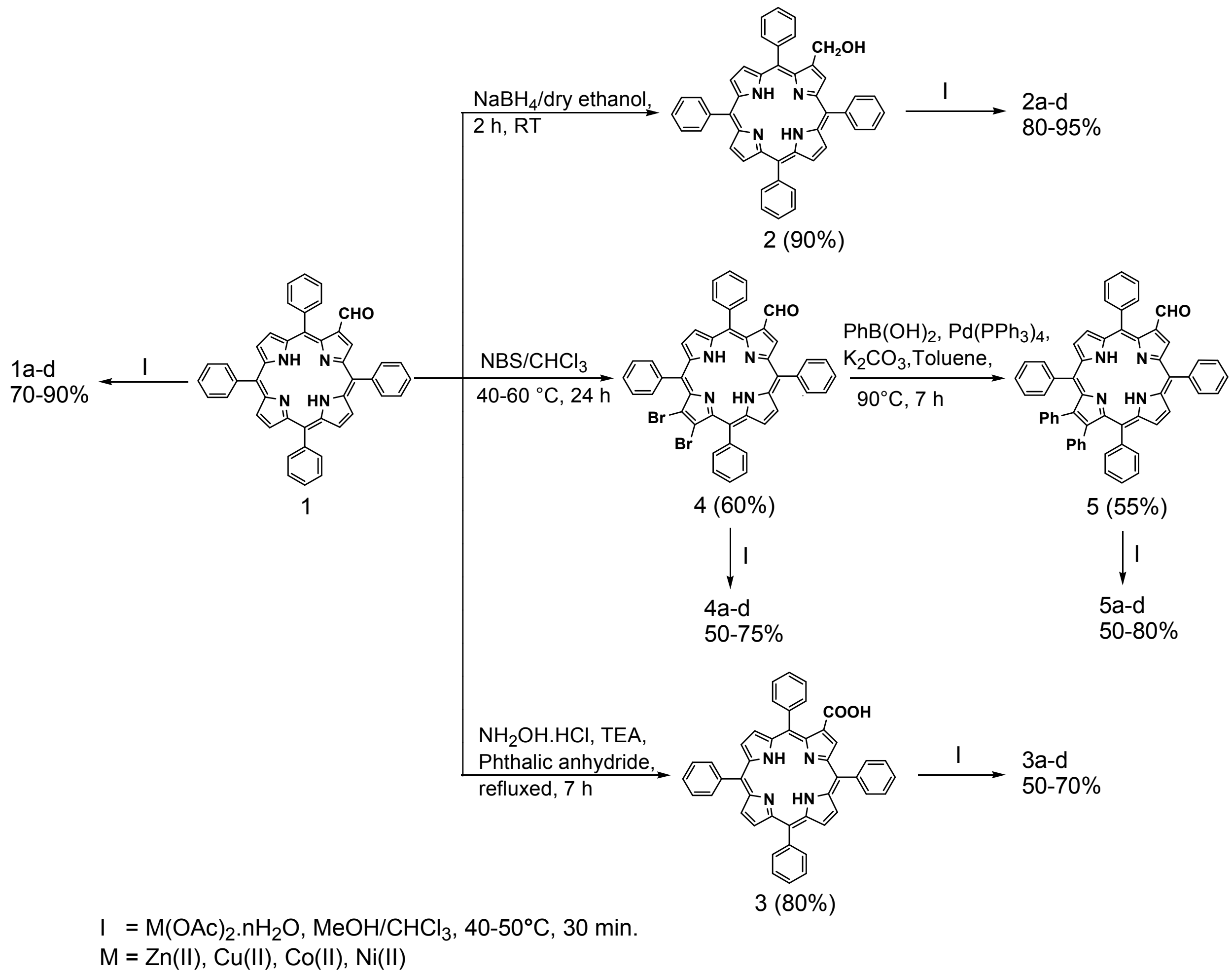
CoTPP.



Scheme S1. Synthetic scheme for $MTPP(X)Y_2$.

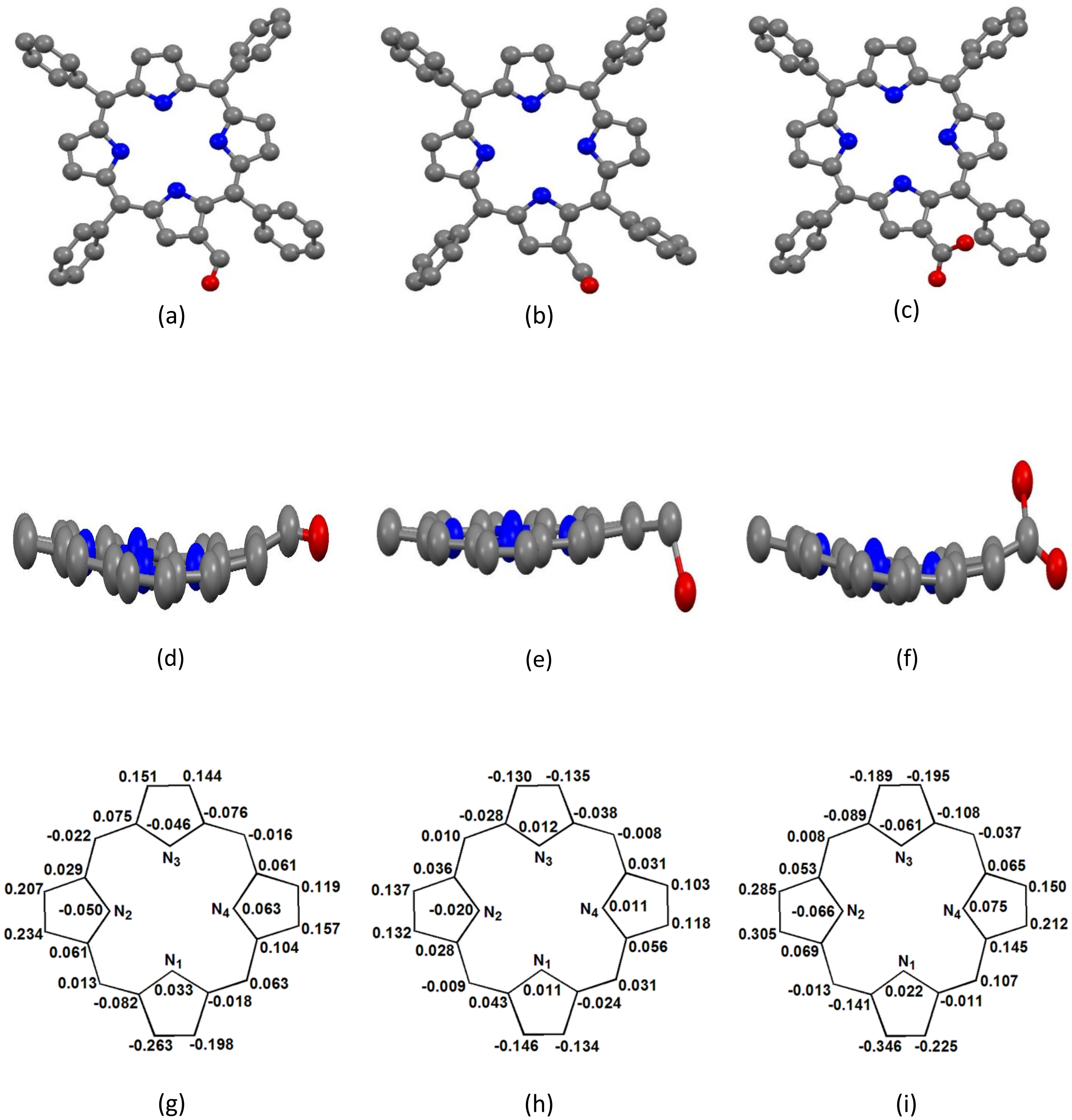


Figure S1. B3LYP/ 6-311g(d,p) optimised geometries showing top as well as side views of **H_2TPP(CHO)** (**a** and **d**), **H_2TPP(CH_2OH) (b and e)** and **H_2TPP(COOH)** (**c** and **f**), respectively. In side view, the *β*-substituents and *meso*-phenyl groups are not shown for clarity. The displacement of porphyrin-core atoms in Å from the mean plane are shown in figures **g, h** and **i** for **H_2TPP(CHO), H_2TPP(CH_2OH)** and **H_2TPP(COOH)** respectively. Color codes for atoms: C (grey), N (blue) and O (red).

Table S1. Selected bond lengths (Å) and bond angles (deg) for the B3LYP/6-311g(d,p) optimised geometries of H2TPP(X)Y_2 (X = CHO, CH2OH and COOH, Y = Br and Ph).

	H_2TPP(CHO)	H_2TPP(CH_2OH)	H_2TPP(COOH)	H_2TPP(CHO)Br_2	H_2TPP(CHO)$(Ph)_2$
			Bond Length (Å)		
N-C_α	1.363	1.364	1.363	1.363	1.362
N′-$C_{\alpha'}$	1.374	1.374	1.374	1.375	1.375
C_α-C_β	1.461	1.461	1.460	1.462	1.465
$C_{\alpha'}$-$C_{\beta'}$	1.433	1.433	1.434	1.433	1.433
C_β-C_β	**1.357**	**1.353**	**1.358**	**1.363**	**1.366**
$C_{\beta'}$-$C_{\beta'}$	1.366	1.366	1.366	1.365	1.366
C_α-C_m	1.410	1.409	1.410	1.414	1.414
$C_{\alpha'}$-C_m	1.401	1.402	1.402	1.403	1.403
ΔC_β (Å)[a]	**0.184**	**0.129**	**0.238**	**0.575**	**0.578**
Δ24 (Å)[b]	**0.095**	**0.059**	**0.123**	**0.266**	**0.256**
			Bond Angle (deg)		
N-C_α-C_m	**125.78**	**125.59**	**125.83**	**124.52**	**124.49**
N′-$C_{\alpha'}$-C_m	126.94	127.06	127.00	127.19	126.81
N-C_α-C_β	110.64	110.62	110.54	109.91	110.59
N′-$C_{\alpha'}$-$C_{\beta'}$	106.45	106.43	106.43	106.29	106.28
C_β- C_α-C_m	**123.54**	**123.74**	**123.52**	**125.47**	**124.98**
$C_{\beta'}$- $C_{\alpha'}$-C_m	126.58	126.49	126.68	126.46	126.70
C_α-C_β-C_β	106.34	106.38	106.38	106.46	106.73
$C_{\alpha'}$-$C_{\beta'}$-$C_{\beta'}$	108.19	108.20	108.20	108.26	108.26
C_α-N-C_α	105.99	105.80	106.08	107.00	106.32
$C_{\alpha'}$-N- $C_{\alpha'}$	110.69	110.72	110.71	110.83	110.88
C_α-C_m-$C_{\alpha'}$	125.36	125.66	125.18	124.73	124.70

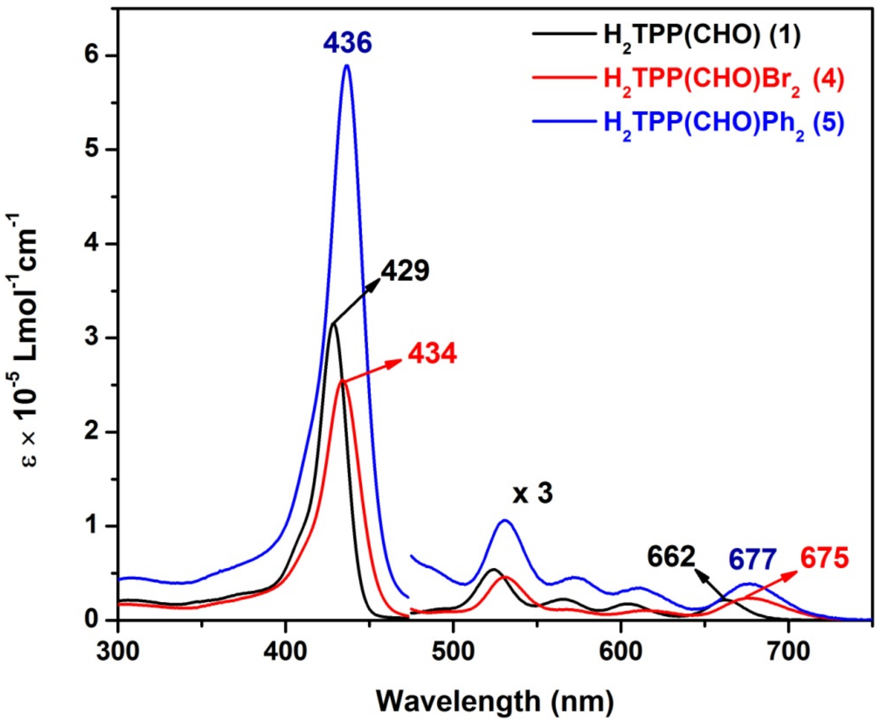


Figure S2. UV-Visible spectra of **1, 4** and **5** in CH_2Cl_2 at 298 K.

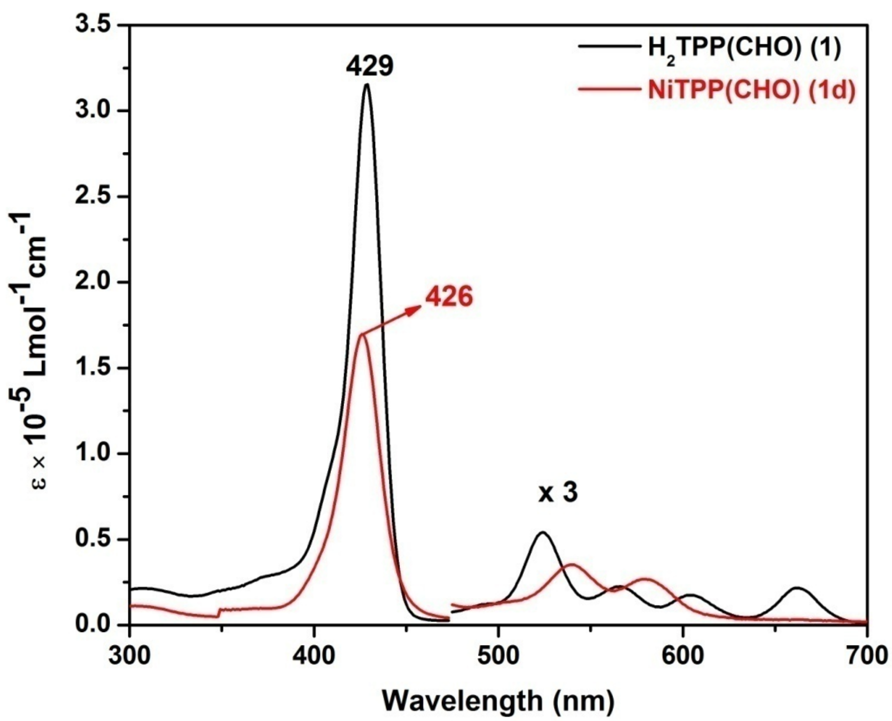


Figure S3. UV-Visible spectra of **1** and **1d** in CH_2Cl_2 at 298 K.

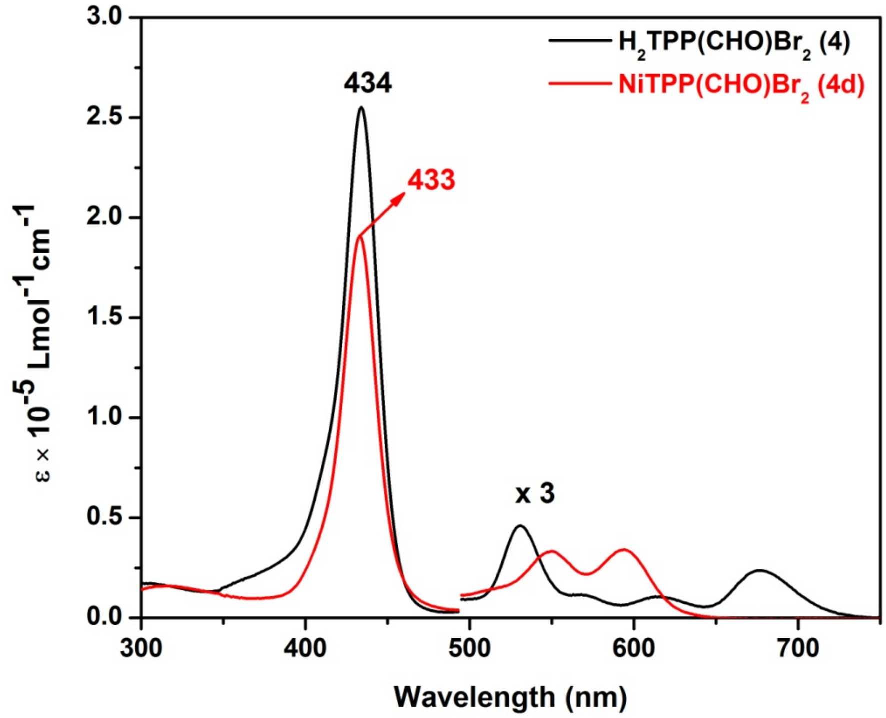


Figure S4. UV-Visible spectra of **4** and **4d** in CH_2Cl_2 at 298 K.

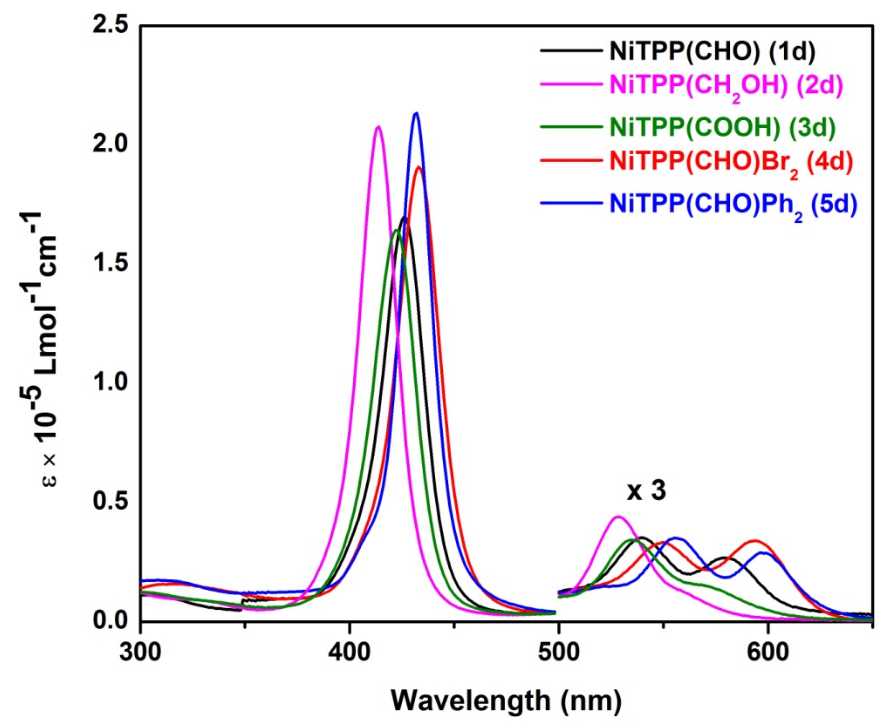


Figure S5. UV-Visible spectra of **1d - 5d** in CH_2Cl_2 at 298 K.

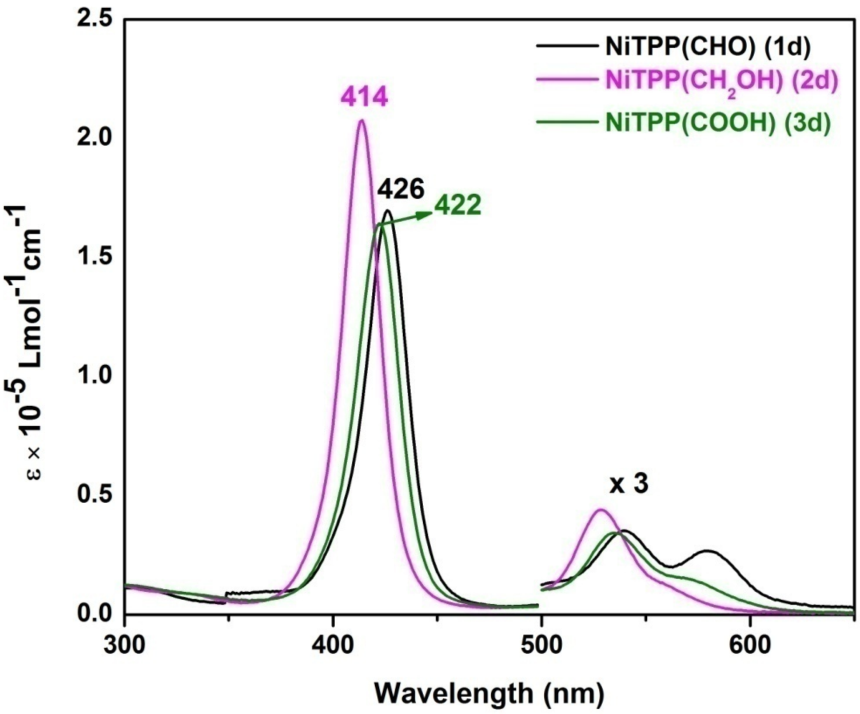


Figure S6. UV-Visible spectra of **1d - 3d** in CH_2Cl_2 at 298 K.

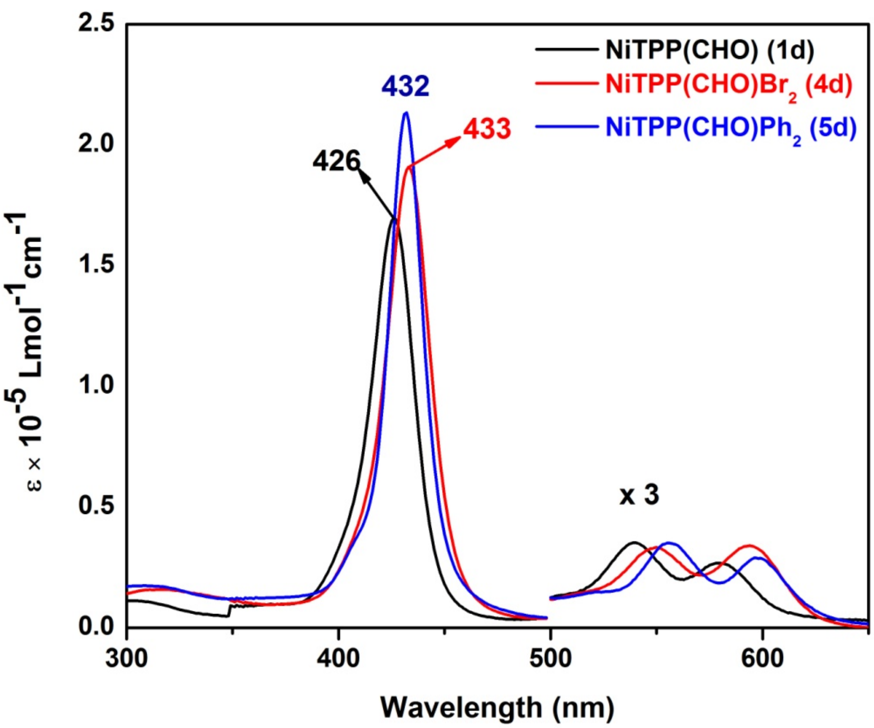


Figure S7. UV-Visible spectra of **1d, 4d** and **5d** in CH_2Cl_2 at 298 K.

Table S2. UV-Vis spectral data of Cu(II), Co(II) and Ni(II) complexes of *β*-mono- and trisubstituted porphyrins in CH_2Cl_2 at 298 K.

Porphyin	**B band, λ_{max},nm**	**Q bands, λ_{max}, nm**
CuTPP(CHO) (**1b**)	426(5.33)	549(3.97),591(3.79)
CuTPP(CH_2OH) (**2b**)	414(5.59)	538(4.23)
CuTPP(COOH) (**3b**)	421(5.48)	545(4.22),581(3.68)
CuTPPBr_2(CHO) (**4b**)	430(5.31)	557(3.98),598(3.95)
CuTPP(Ph_2)(CHO) (**5b**)	432(5.33)	556(4.04),597(3.97)
CoTPP(CHO) (**1c**)	422(4.80)	539(3.51),577(3.38)
CoTPP(CH_2OH) (**2c**)	409(5.38)	528(4.14)
CoTPP(COOH) (**3c**)	416(5.23)	535(4.04)
CoTPPBr_2(CHO) (**4c**)	428(5.18)	549(3.98),589(4.0)
CoTPP(Ph_2)(CHO) (**5c**)	429(4.96)	550(3.81),587(3.80)
NiTPP(CHO) (**1d**)	426(5.22)	540(4.06),580(3.94)
NiTPP(CH_2OH) (**2d**)	414(5.31)	529(4.16)
NiTPP(COOH) (**3d**)	422(5.21)	535(4.05),561(sh)
NiTPPBr_2(CHO) (**4d**)	430(5.27)	550(4.03),594(4.04)
NiTPP(Ph_2)(CHO) (5**d**)	432(5.32)	556(4.06),596(3.98)

[a]The values in parentheses refer to logε values, ε in dm^3/mol/cm; Por = Porphyrin; sh = shoulder.

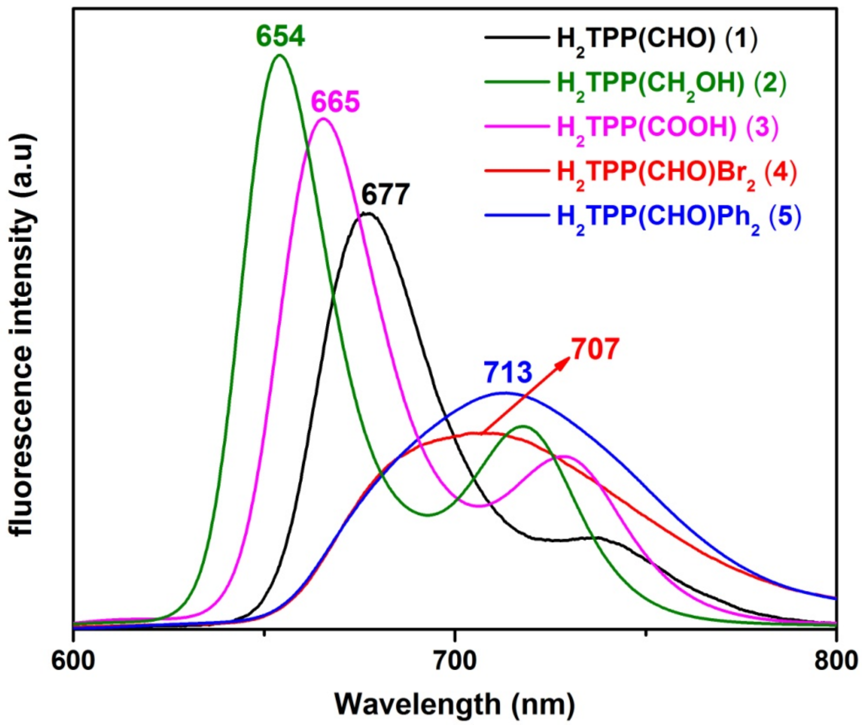


Figure S8. Fluorescence spectra of **1 - 5** in CH_2Cl_2 at 298 K.

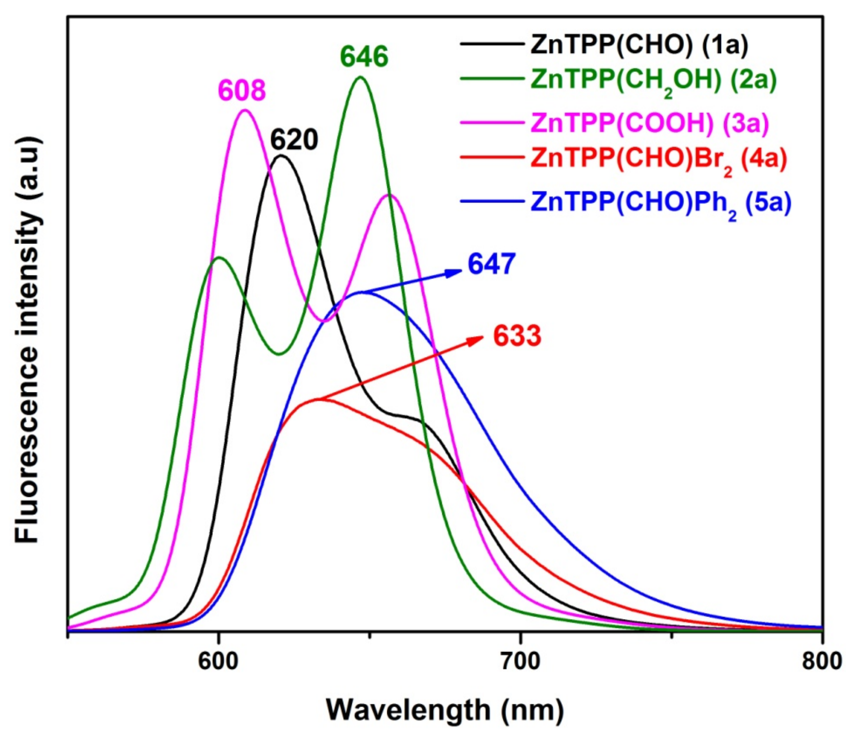


Figure S9. Fluorescence spectra of **1a - 5a** in CH_2Cl_2 at 298 K.

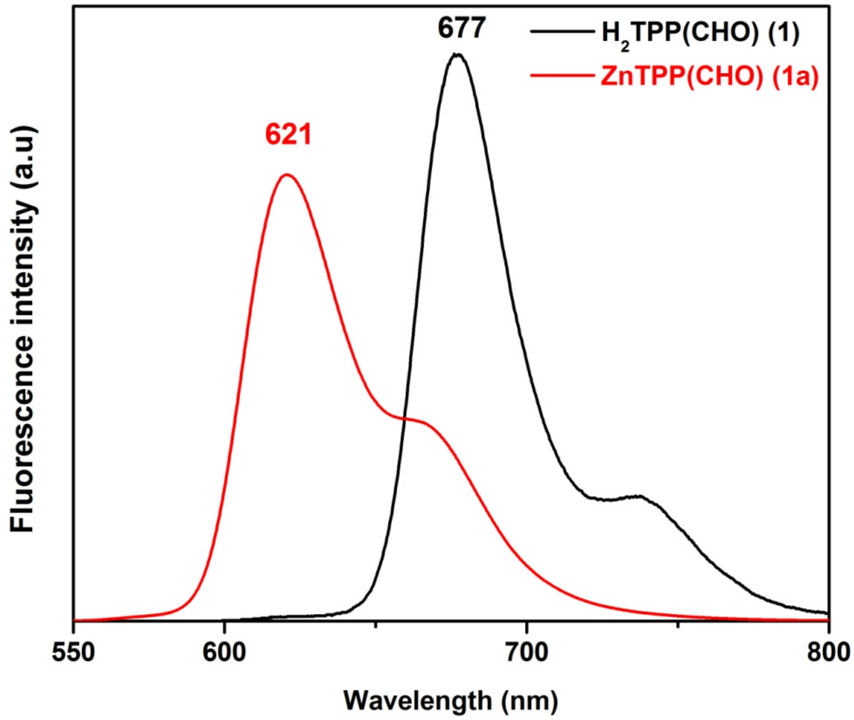


Figure S10. Fluorescence spectra of **1** and **1a** in CH_2Cl_2 at 298 K.

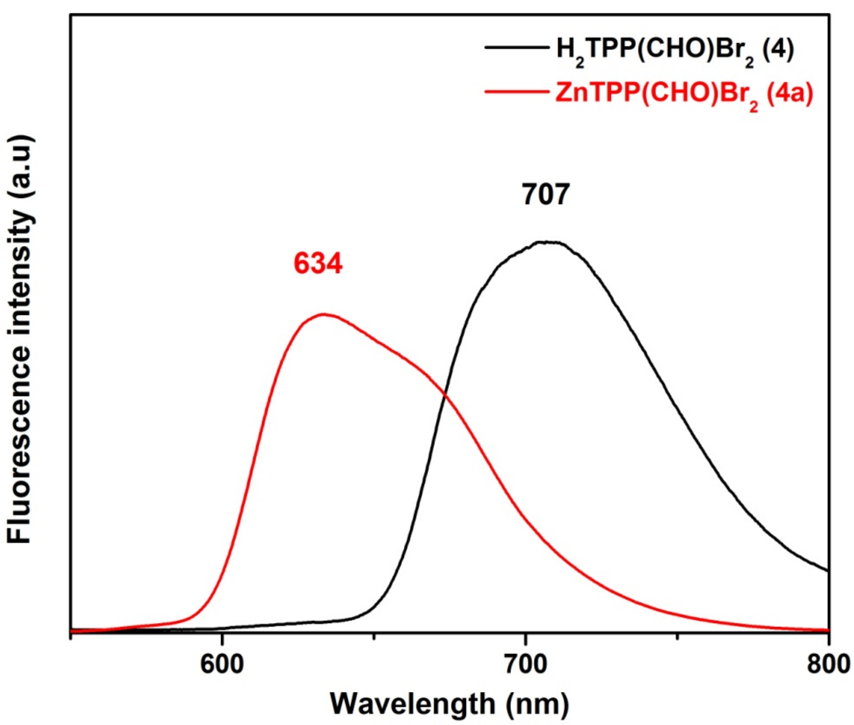


Figure S11. Fluorescence spectra of **4** and **4a** in CH_2Cl_2 at 298 K.

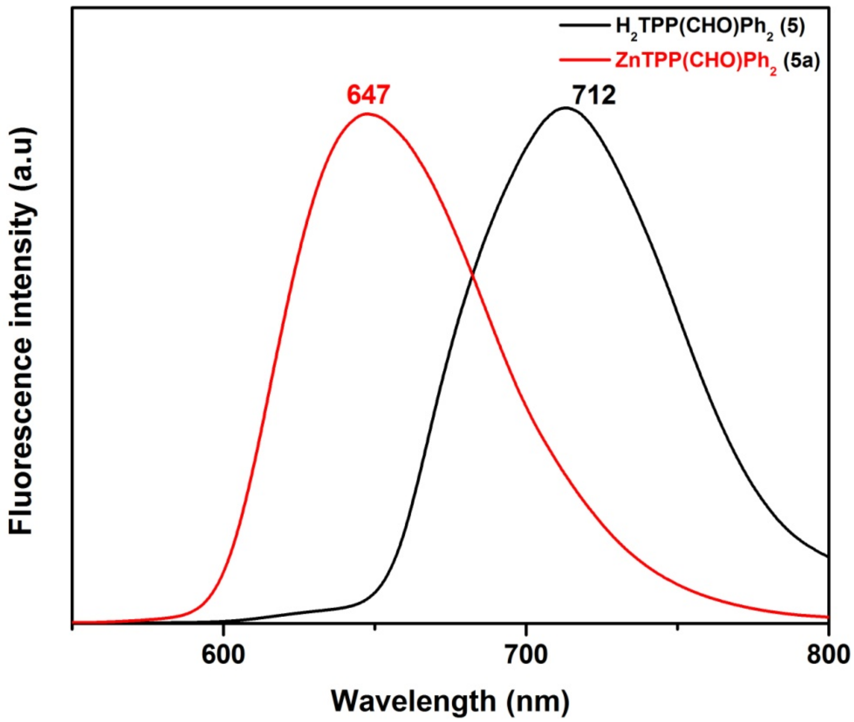


Figure S12. Fluorescence spectra of **5** and **5a** in CH_2Cl_2 at 298 K.

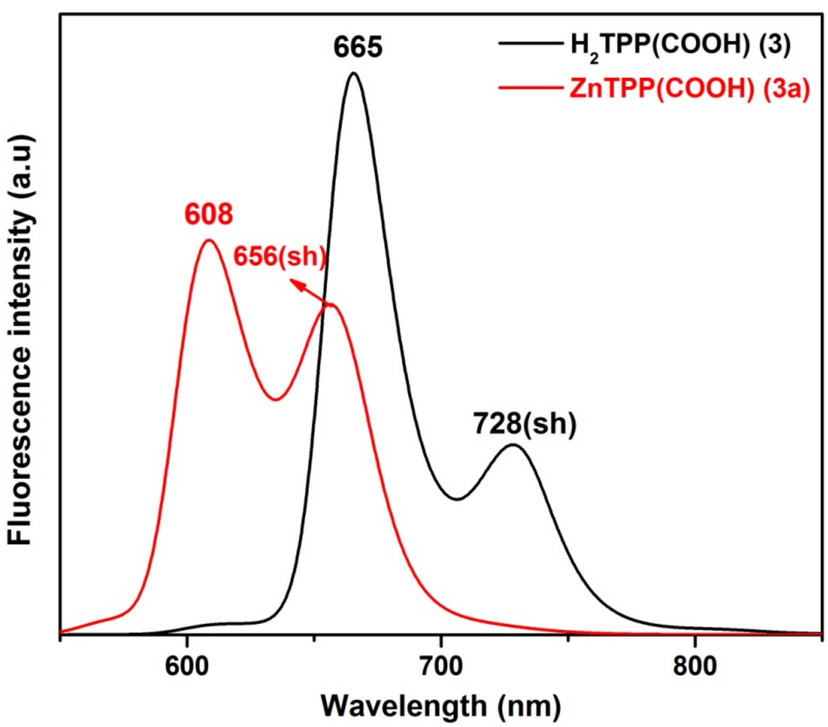


Figure S13. Fluorescence spectra of **3** and **3a** in CH_2Cl_2 at 298 K.

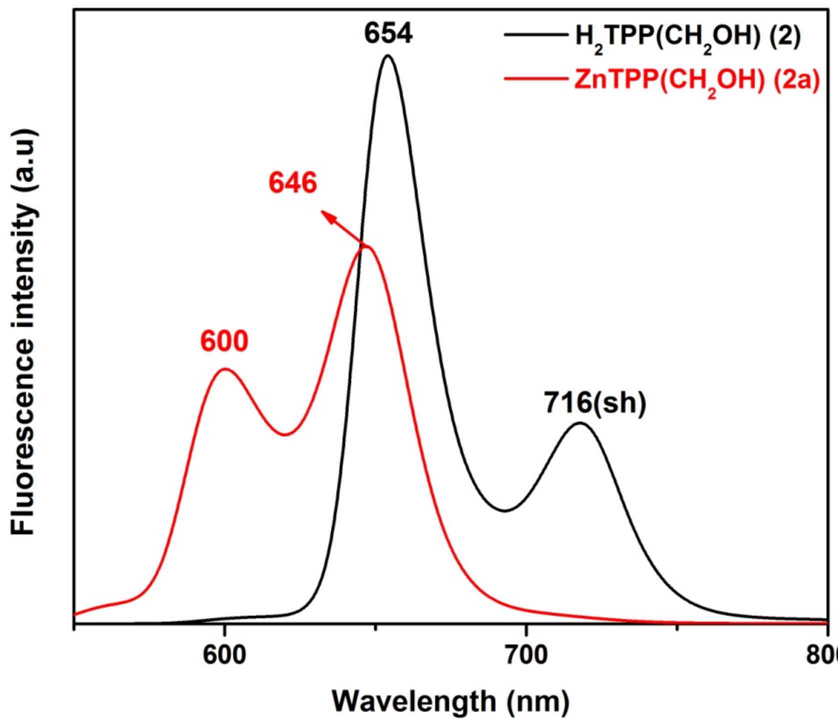


Figure S14. Fluorescence spectra of **2** and **2a** in CH_2Cl_2 at 298 K.

Table S3. Fluorescence Spectral data of mono/tri-*β*-substituted porphyrins in CH_2Cl_2 at 298 K.

Porphyrin	λ_{Ex}nm	$\lambda_{fl,max}$nm	Quantum Yield, ϕ_f^a	Stokes shift (nm)	Stokes shift (cm^{-1})
1	429	677	0.1420 ± 0.0030	15	334
2	417	654	0.1132 ± 0.0020	9	213
3	423	665	0.0913 ± 0.0021	13	300
4	434	707	0.0025 ± 0.0003	32	670
5	436	713	0.0560 ± 0.0018	36	746
1a	430	620	0.0209 ± 0.0011	19	509
2a	418	606	0.0266 ± 0.0013	53	1615
3a	425	608	0.0279 ± 0.0009	16	444
4a	434	633	0.0009 ± 0.00001	27	704
5a	436	647	0.0091 ± 0.0004	41	1046

$^a\phi_f$ were calculated using literature method (E. Austin and M. Gouterman, *Bioinorg. Chem*. 1978, **9**, 281).

Fluorescence quantum yield are determined by the comparative method.[1-2]

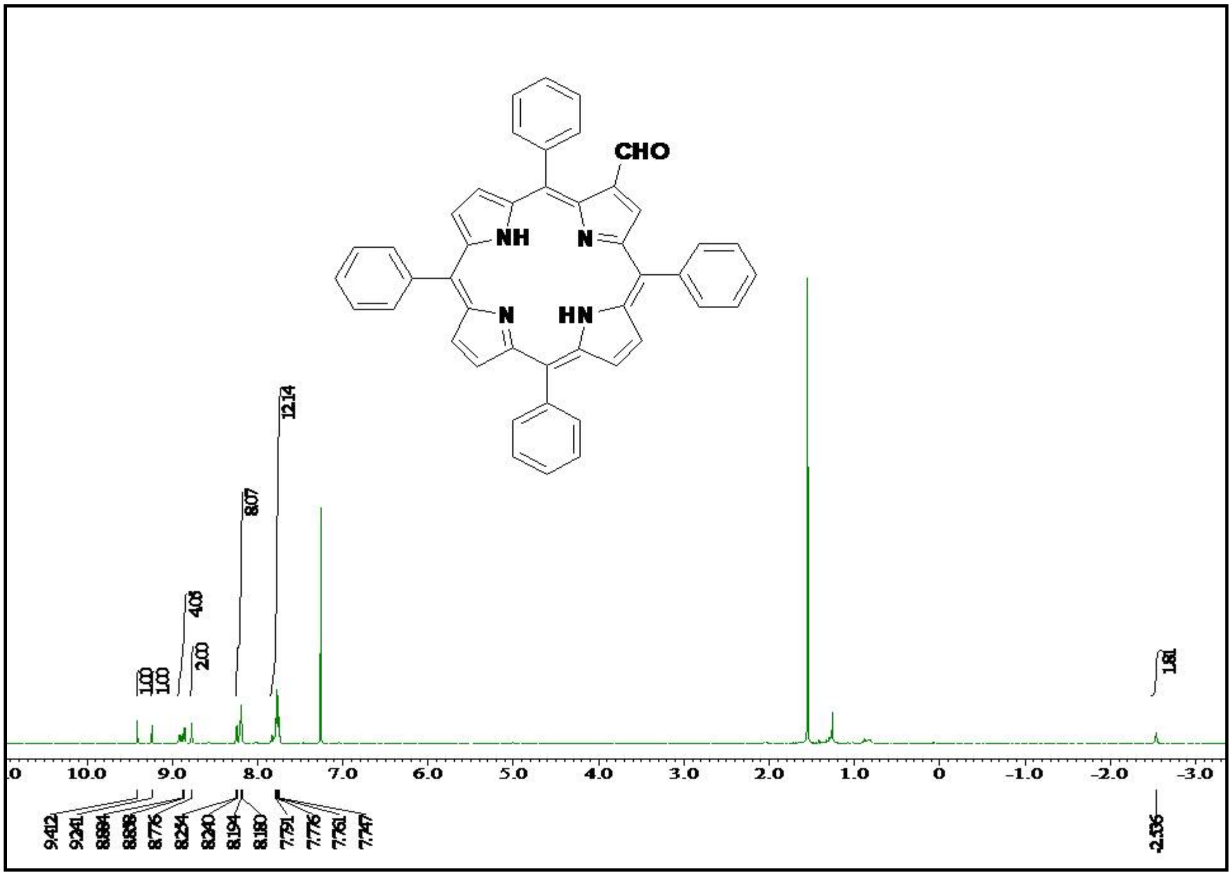


Figure S15.[1]H NMR spectrum of **1** in $CDCl_3$ at 298 K.

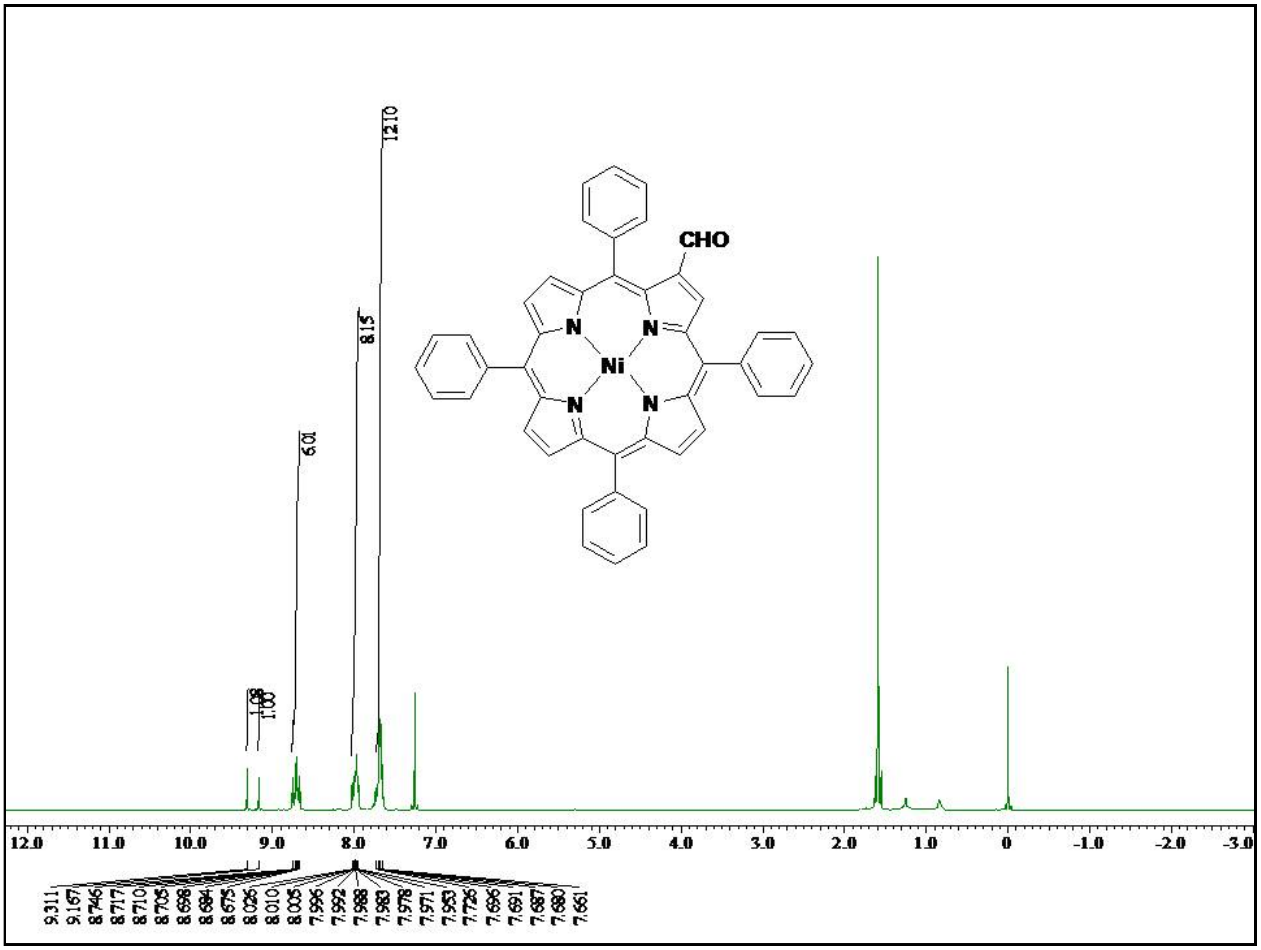


Figure S16.[1]H NMR spectrum of **1d** in $CDCl_3$ at 298 K.

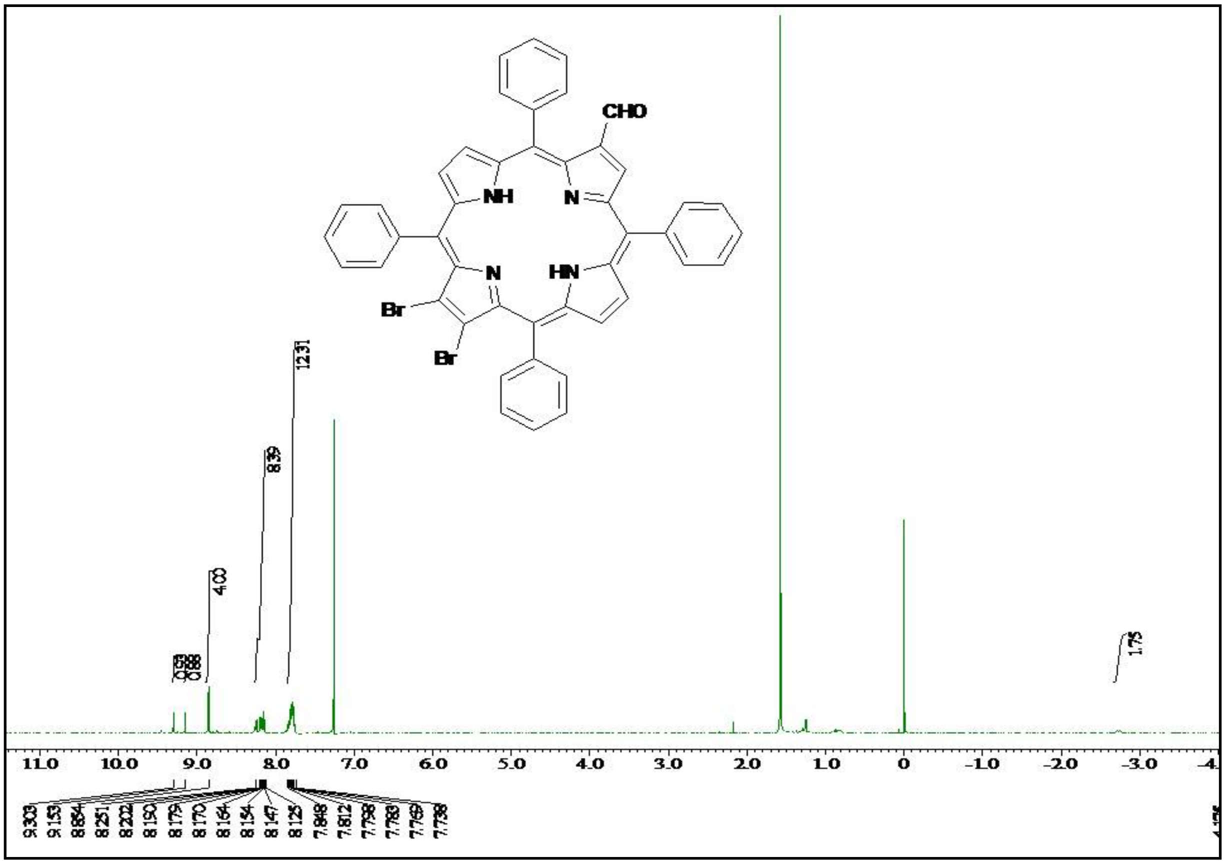


Figure S17.[1]H NMR spectrum of **4** in $CDCl_3$ at 298 K.

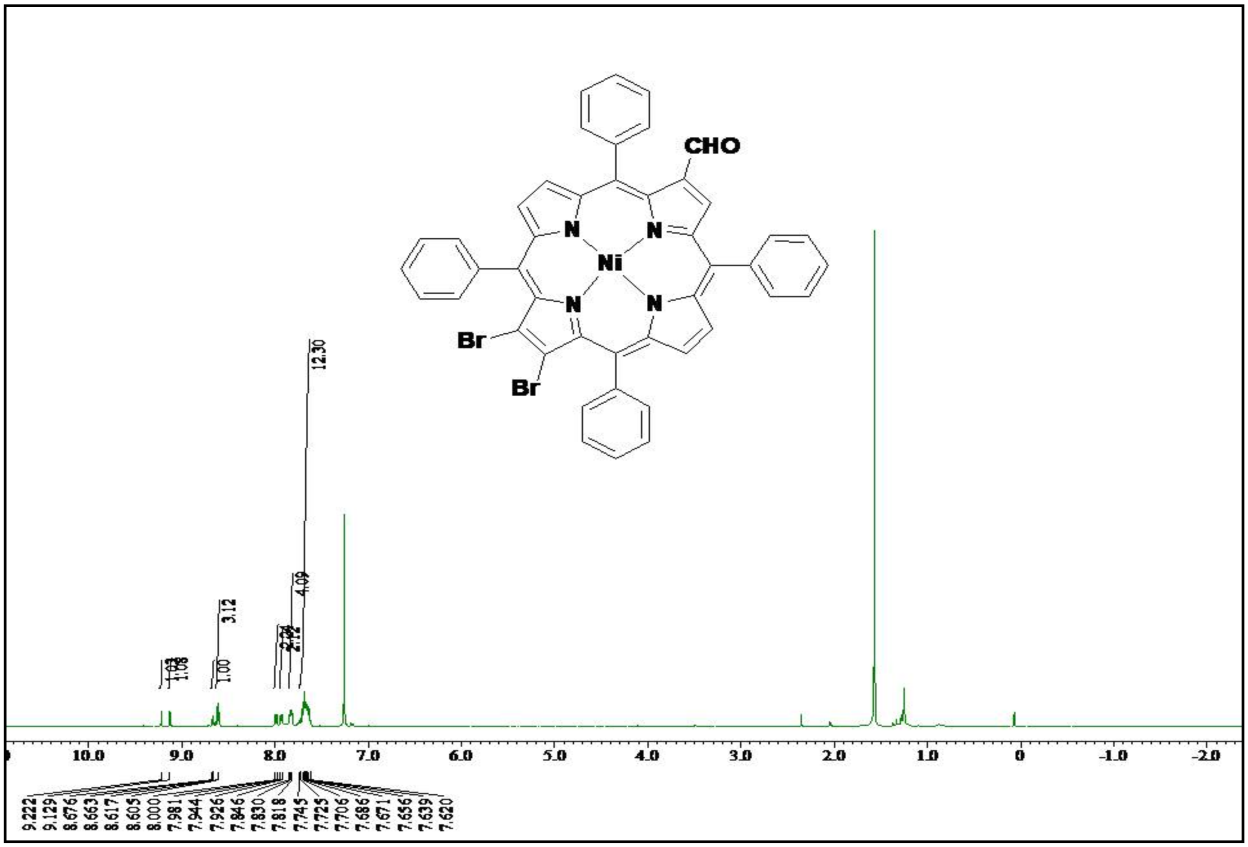


Figure S18. ^{1}H NMR spectrum of **4d** in $CDCl_3$ at 298 K.

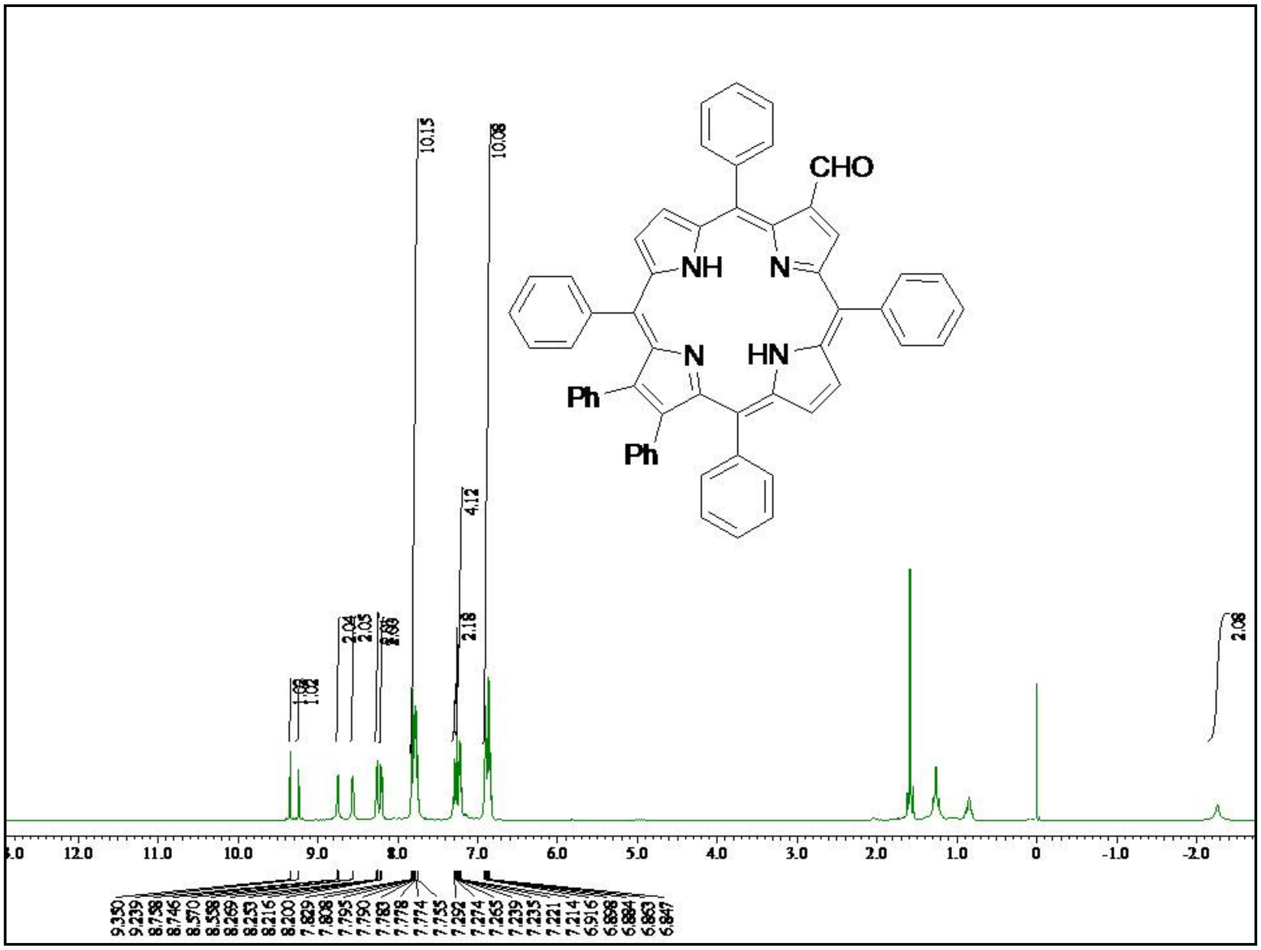


Figure S19. ^{1}H NMR spectrum of **5** in $CDCl_3$ at 298 K.

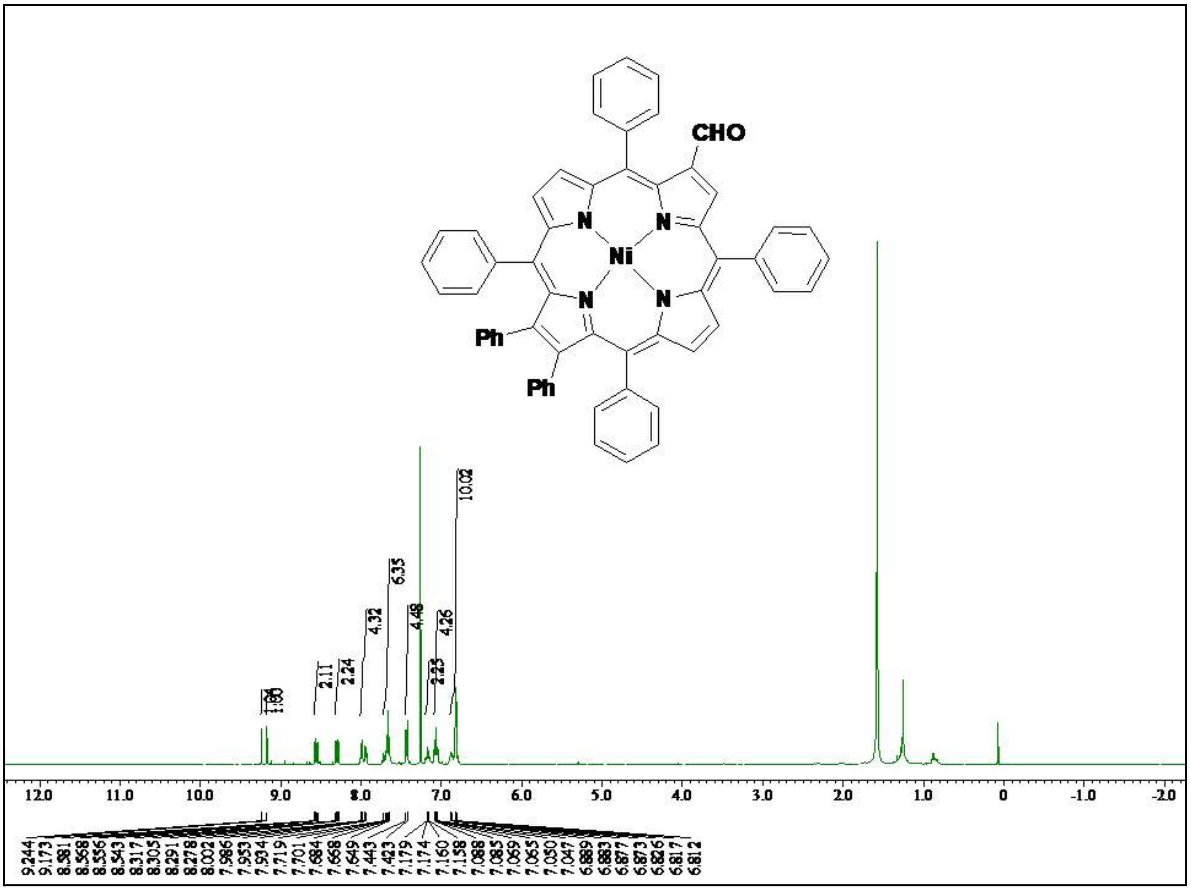


Figure S20.[1]H NMR spectrum of **5d** in $CDCl_3$ at 298 K.

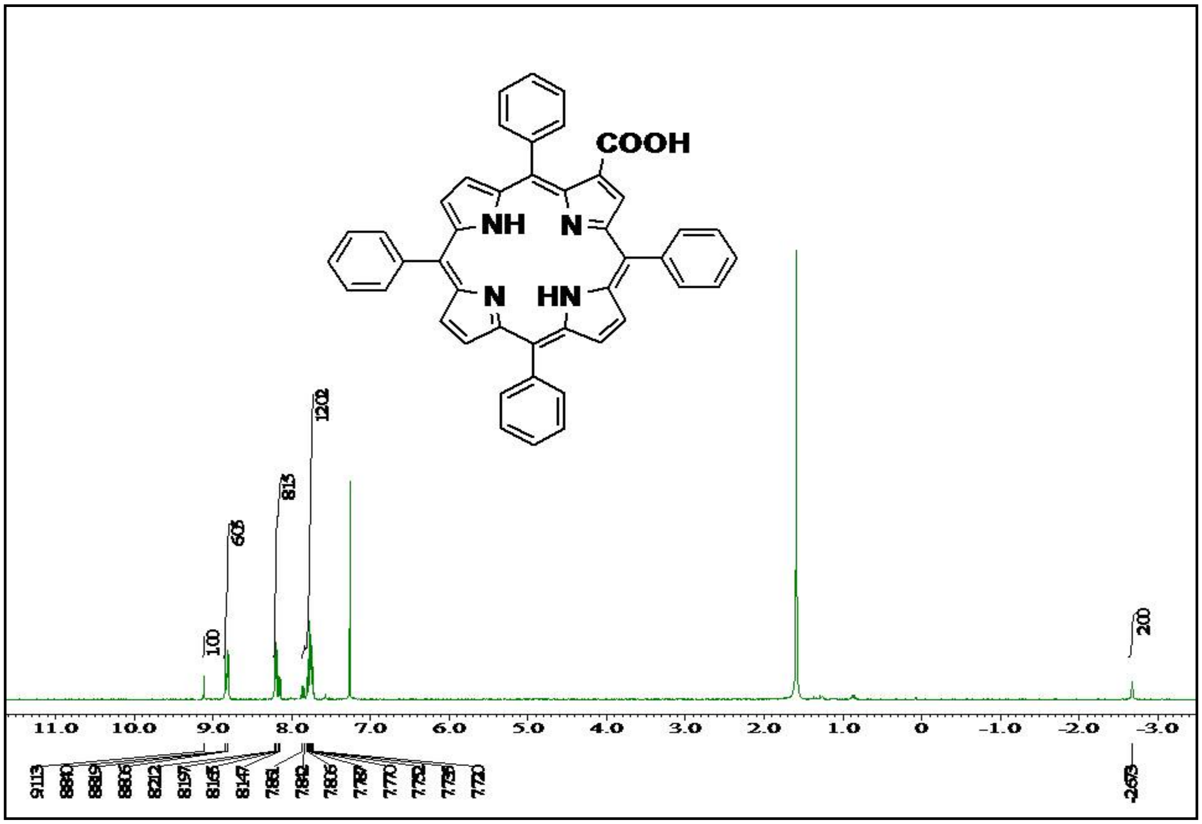


Figure S21.[1]H NMR spectrum of **3** in $CDCl_3$ at 298 K

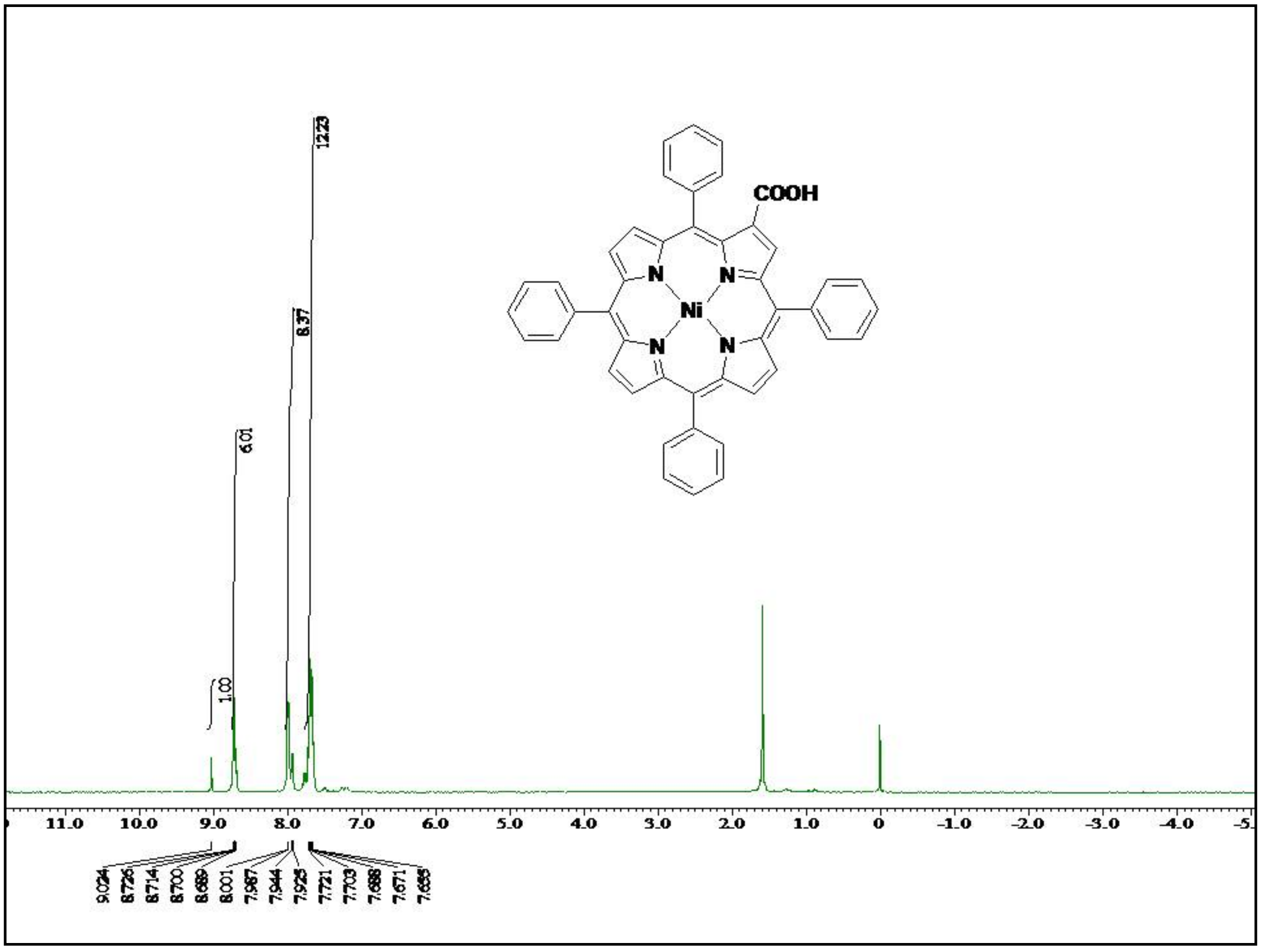


Figure S22.[1]H NMR spectrum of **3d** in $CDCl_3$ at 298 K.

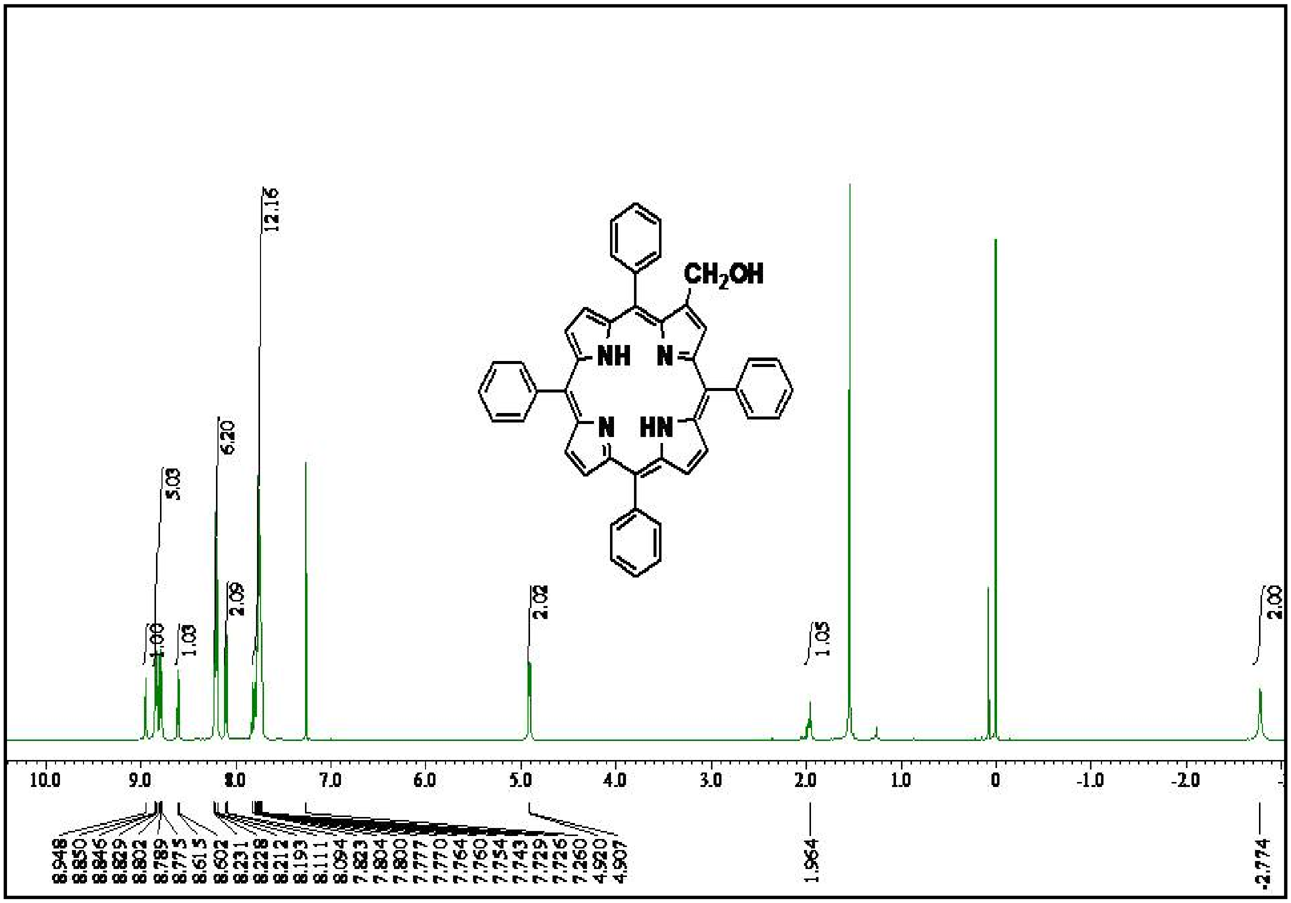


Figure S23.[1]H NMR spectrum of **2** in $CDCl_3$ at 298 K

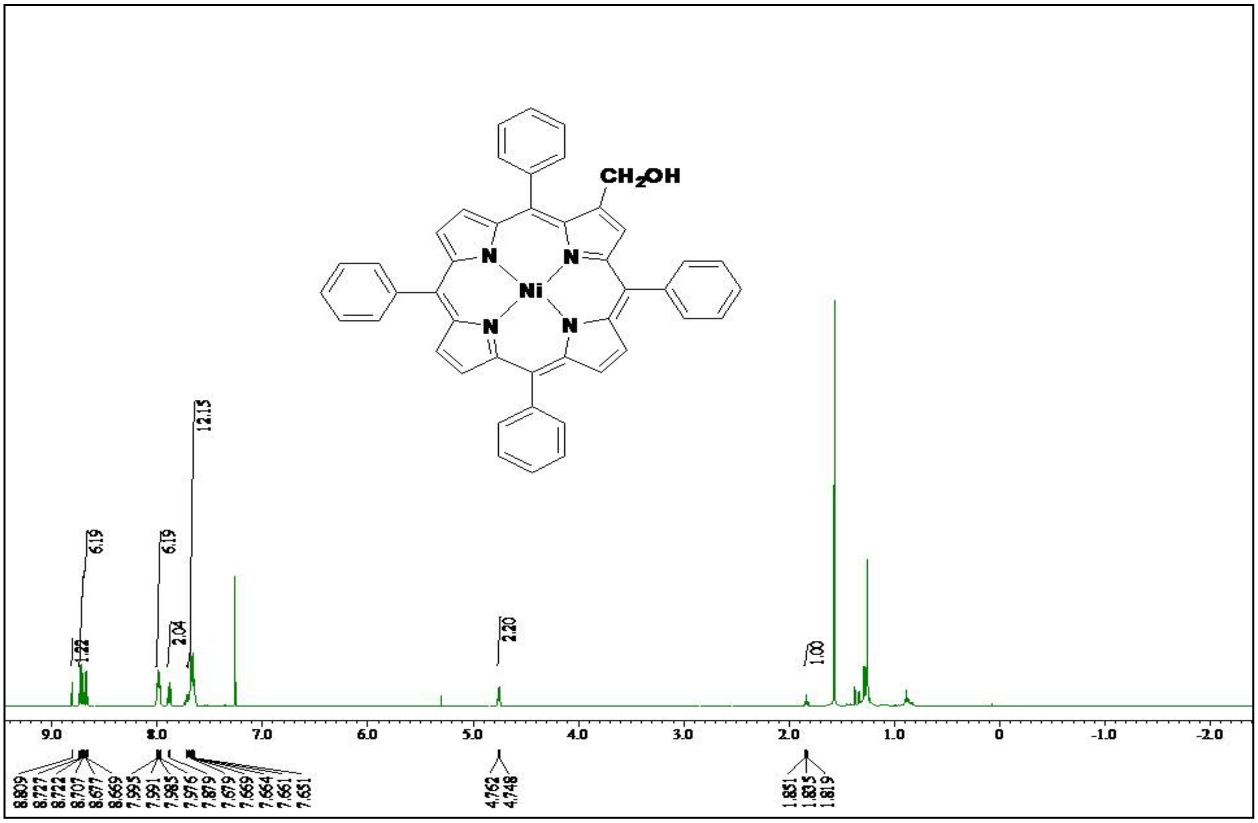


Figure S24. ^{1}H NMR spectrum of **2d** in $CDCl_3$ at 298 K.

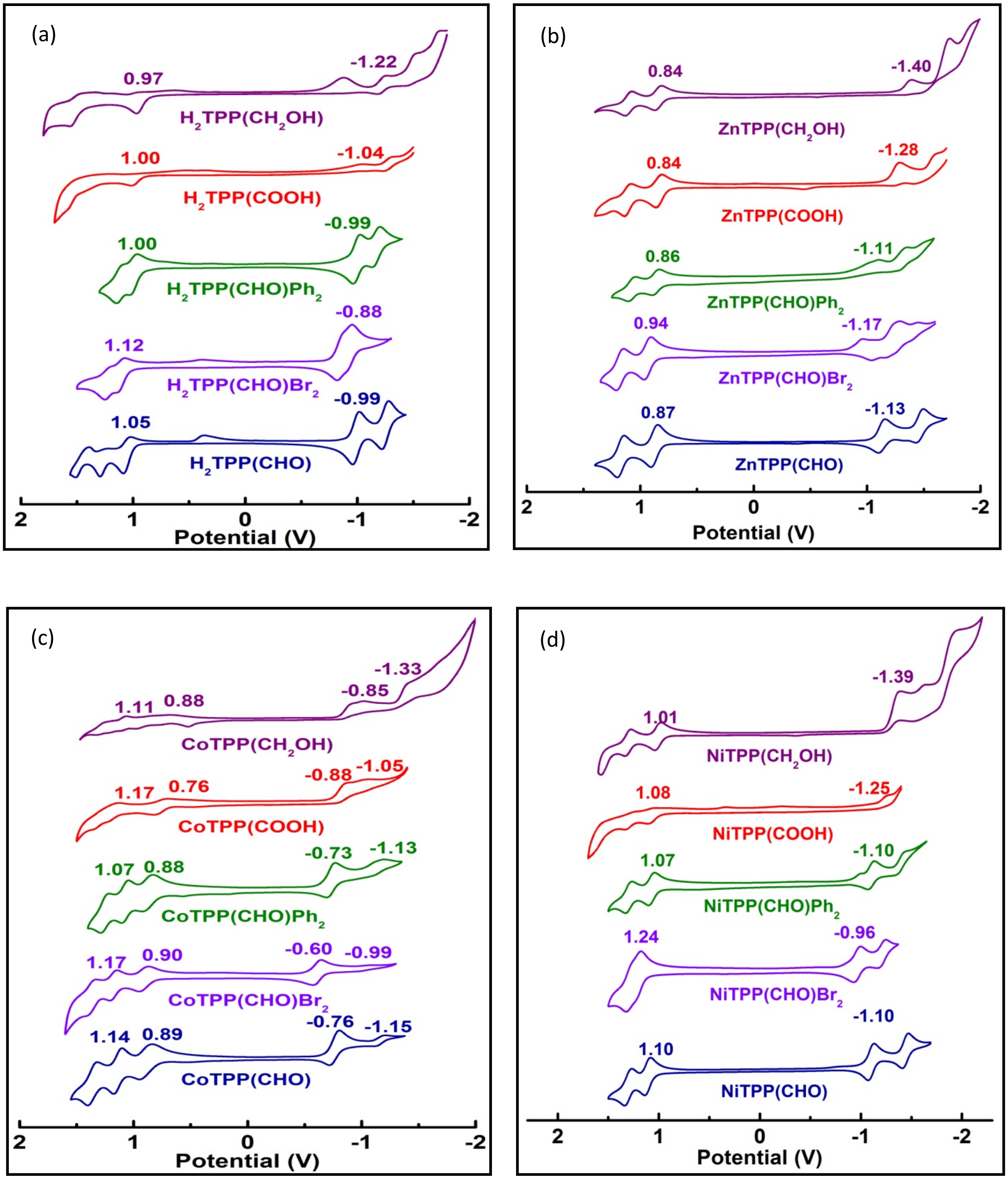
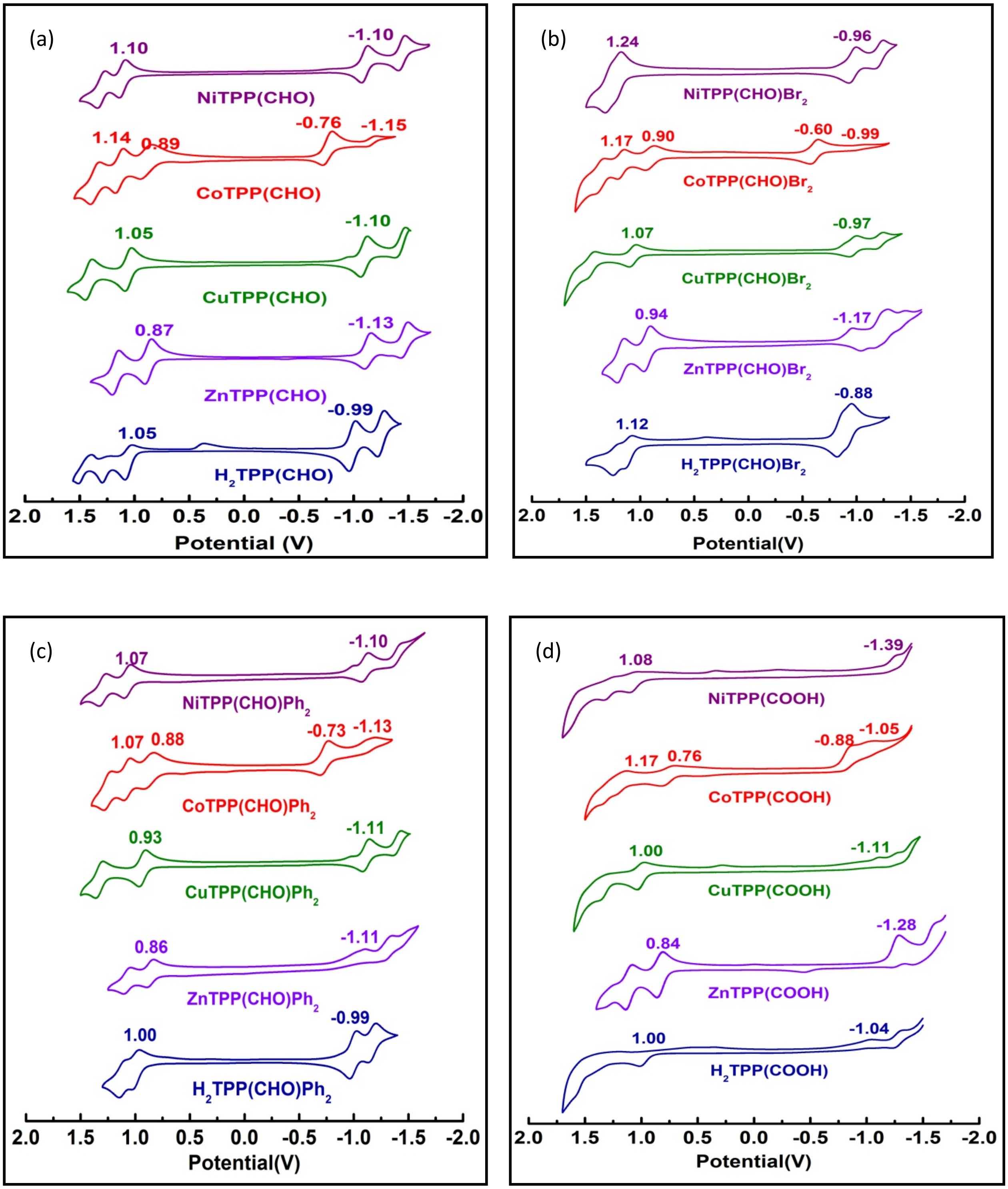


Figure S25. Cyclic voltammograms of (a) $H_2TPP(X)Y_2$, (b) $ZnTPP(X)Y_2$ (c) $CoTPP(X)Y_2$ (d) $NiTPP(X)Y_2$ (where X = CHO, COOH, CH_2OH and Y = H, Br, Ph) complexes in CH_2Cl_2.


(a)
1.10
-1.10
NiTPP(CHO)
1.14
0.89
-0.76
-1.15
CoTPP(CHO)
1.05
-1.10
CuTPP(CHO)
0.87
-1.13
ZnTPP(CHO)
1.05
-0.99
H2TPP(CHO)
2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
Potential (V)
(b)
1.24
-0.96
NiTPP(CHO)Br2
1.17
0.90
-0.60
-0.99
CoTPP(CHO)Br2
1.07
-0.97
CuTPP(CHO)Br2
0.94
-1.17
ZnTPP(CHO)Br2
1.12
-0.88
H2TPP(CHO)Br2
2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
Potential(V)
(c)
1.07
-1.10
NiTPP(CHO)Ph2
1.07
0.88
-0.73
-1.13
CoTPP(CHO)Ph2
0.93
-1.11
CuTPP(CHO)Ph2
0.86
-1.11
ZnTPP(CHO)Ph2
1.00
-0.99
H2TPP(CHO)Ph2
2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
Potential(V)
(d)
1.08
-1.39
NiTPP(COOH)
1.17
0.76
-0.88
-1.05
CoTPP(COOH)
1.00
-1.11
CuTPP(COOH)
0.84
-1.28
ZnTPP(COOH)
1.00
-1.04
H2TPP(COOH)
2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
Potential(V)

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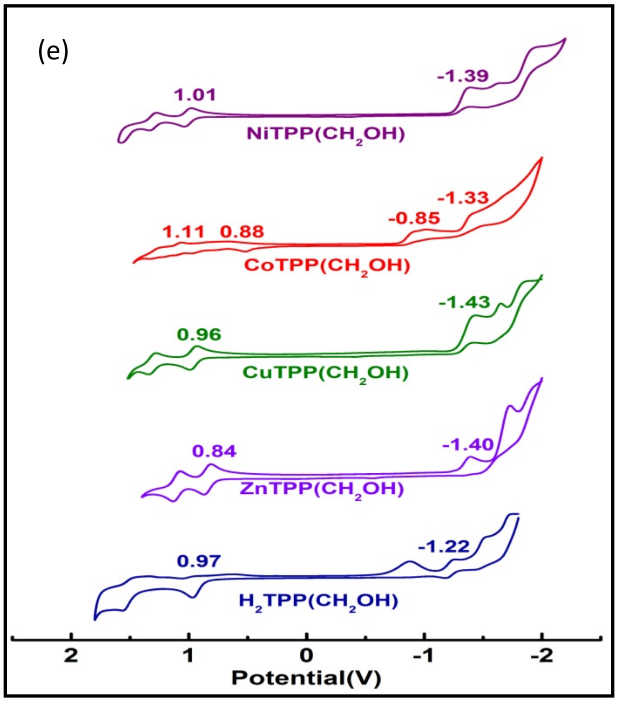
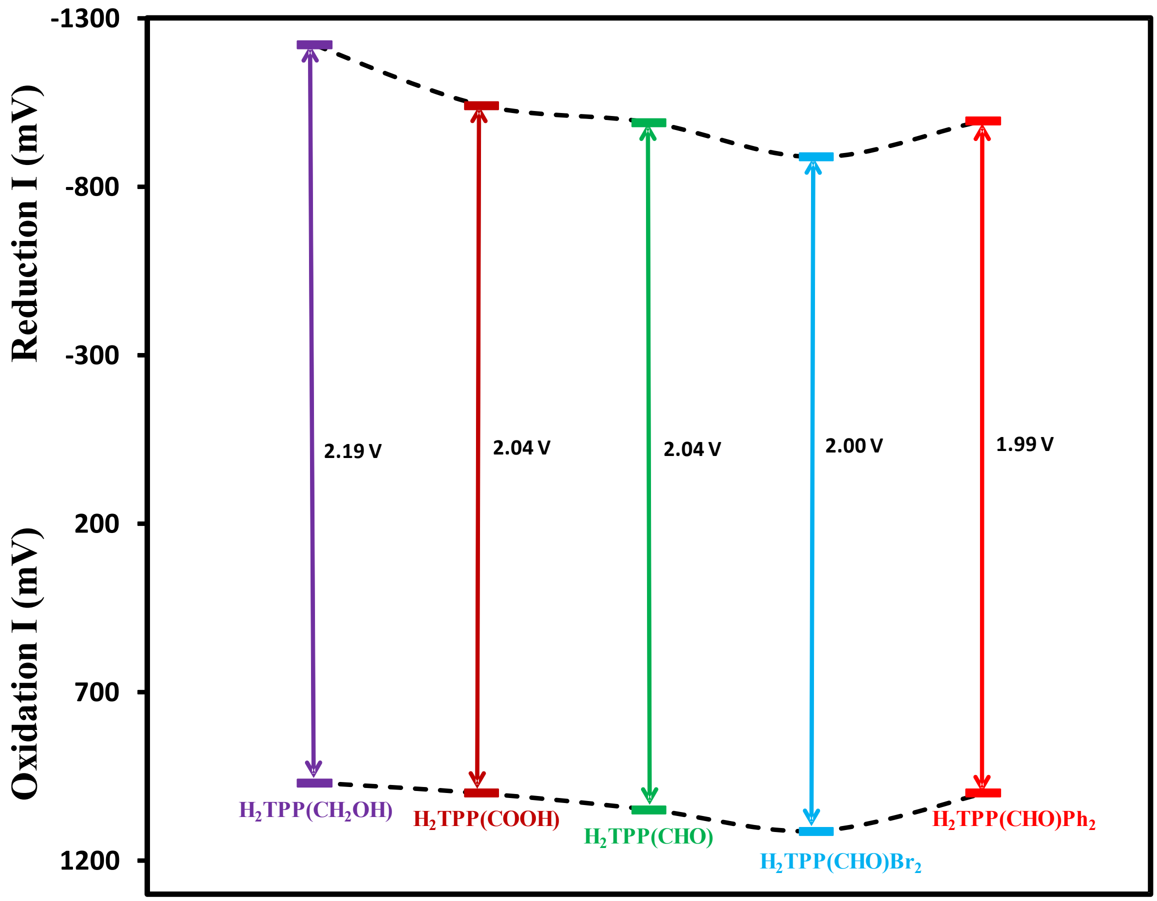


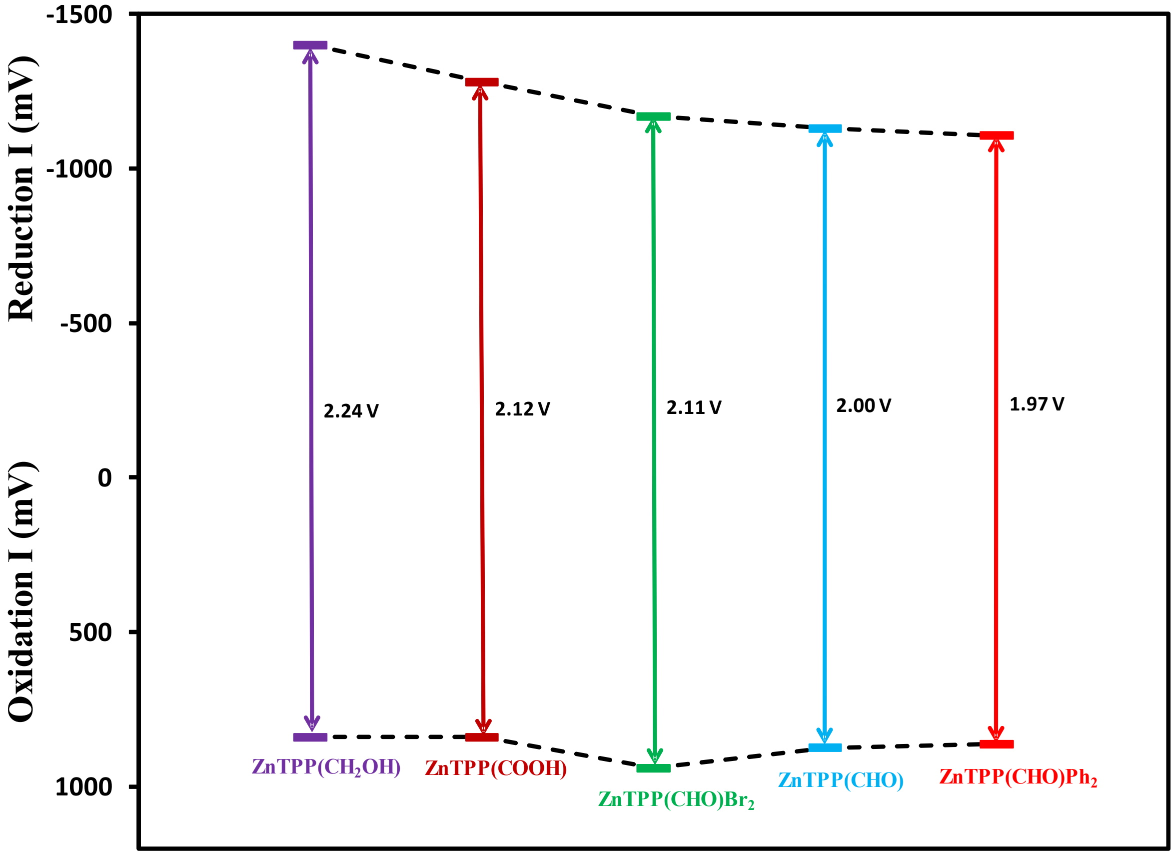
Figure S26. Cyclic voltammograms of (a) MTPP(CHO), (b) MTPP(CHO)Br_2, (c) MTPP(CHO)Ph_2 (d) MTPP(COOH), (e) MTPP(CH_2OH) (where M = 2H, Zn, Cu, Co, Ni) complexes in CH_2Cl_2.

[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



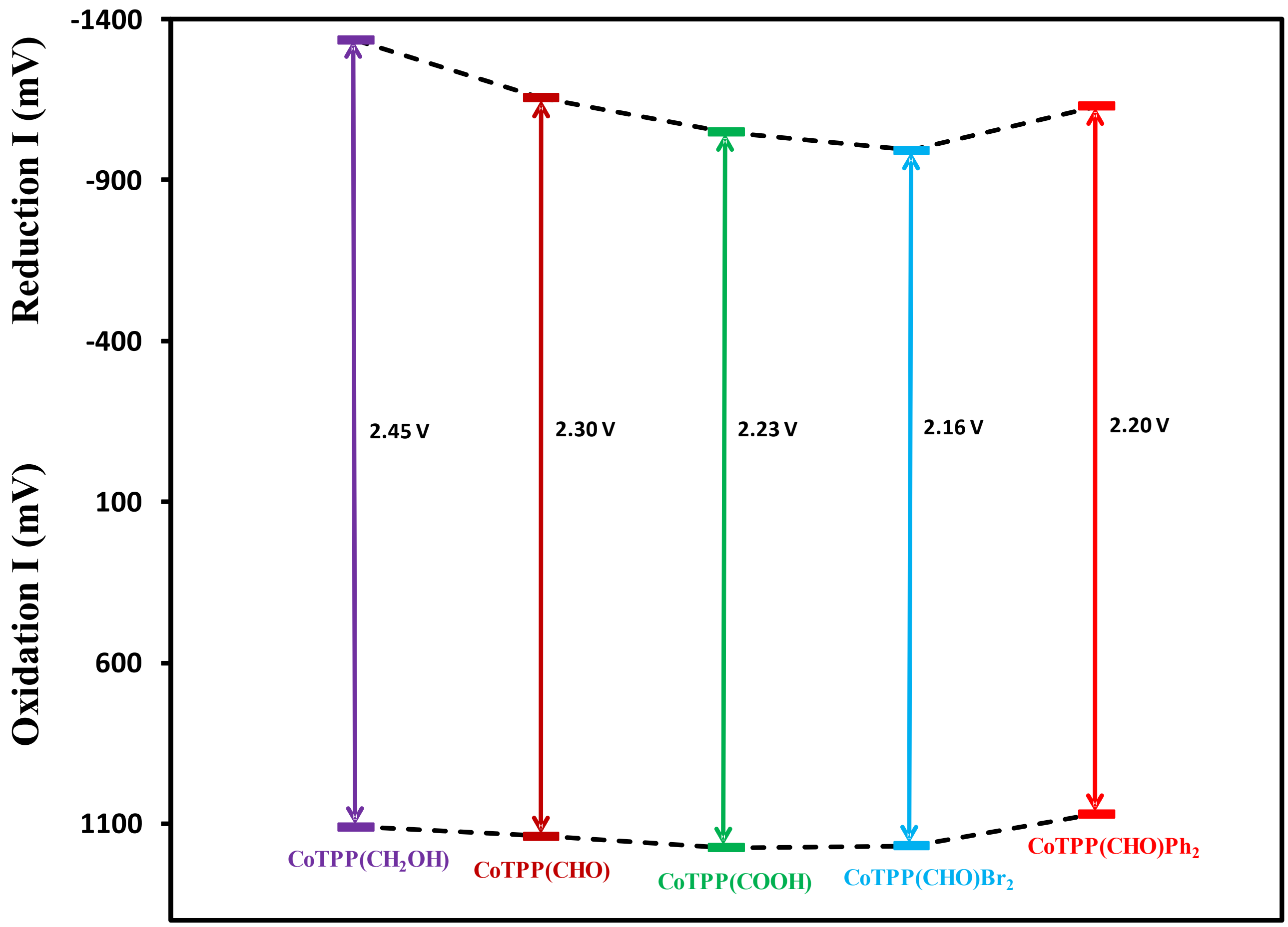
-1300
-800
-300
200
700
1200
Reduction I (mV)
Oxidation I (mV)
2.19 V
2.04 V
2.04 V
2.00 V
1.99 V
H2TPP(CH2OH)
H2TPP(COOH)
H2TPP(CHO)
H2TPP(CHO)Br2
H2TPP(CHO)Ph2

(a) $H_2TPP(X)Y_2$[a]



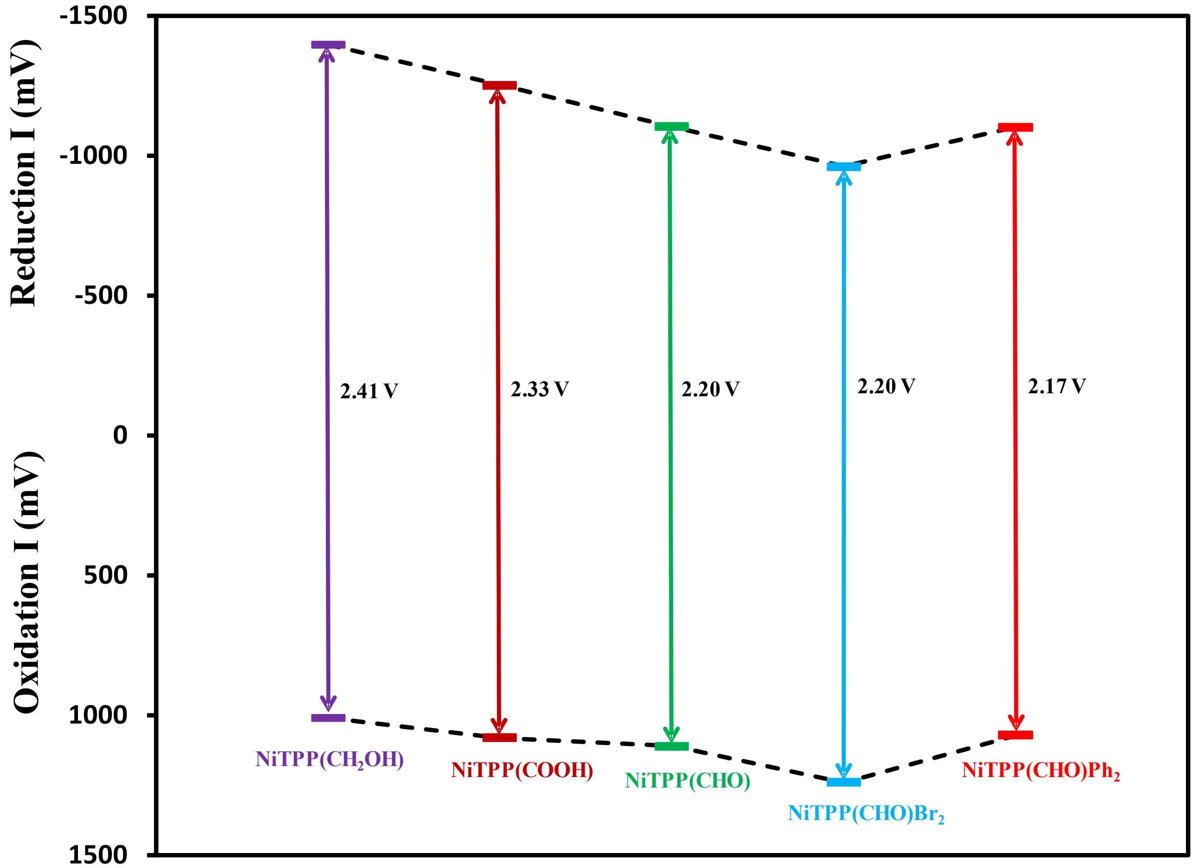
Reduction I (mV)
Oxidation I (mV)
-1500
-1000
-500
0
500
1000
2.24 V
2.12 V
2.11 V
2.00 V
1.97 V
ZnTPP(CH2OH)
ZnTPP(COOH)
ZnTPP(CHO)Br2
ZnTPP(CHO)
ZnTPP(CHO)Ph2

(b) ZnTPP(X)Y_2[a]



Reduction I (mV)
Oxidation I (mV)
-1400
-900
-400
100
600
1100
2.45 V
2.30 V
2.23 V
2.16 V
2.20 V
CoTPP(CH2OH)
CoTPP(CHO)
CoTPP(COOH)
CoTPP(CHO)Br2
CoTPP(CHO)Ph2

(c) $CoTPP(X)Y_2$[a]



(d) NiTPP(X)Y_2[a]

Figure S27. The HOMO-LUMO variation of various Mixed β-substituted porphyrins: (a) $H_2TPP(X)Y_2$ (b) $ZnTPP(X)Y_2$ (c) $CoTPP(X)Y_2$ (d) $NiTPP(X)Y_2$ (where X = CHO, COOH, CH_2OH and Y = H, Br, Ph)

[a] where X = CHO, COOH, CH_2OH and Y = H, Br, Ph.

Table S4. Modulation of frontier and subfrontier orbitals of $CuTPP(X)Y_2$ w.r.t CuTPP.

Por.	E_{cg} (eV)	I_{Ox}	I_{Red}	ΔE*(eV)			$\delta\epsilon_j$ (eV)	$\delta\epsilon_i$ (eV)	$\delta\epsilon_k$ (eV)
				ΔE_{cg}	ΔI_{Ox}	ΔI_{Red}			
CuTPP	2.58	0.97	-1.3	-	-	-	-	-	-
1b	2.50	1.06	-1.1	-0.08	0.09	0.20	-0.09	-0.15	-0.20
2b	2.65	0.96	-1.43	0.07	-0.01	-0.13	0.01	0.12	0.13
3b	2.53	1.00	-1.11	-0.05	0.03	0.19	-0.03	-0.26	-0.19
4b	2.47	1.07	-1.1	-0.11	0.10	0.20	-0.10	-0.09	-0.20
5b	2.47	0.93	-1.11	-0.11	-0.03	0.19	0.04	-0.19	-0.19

Table S5. Modulation of frontier and subfrontier orbitals of $ZnTPP(X)Y_2$ w.r.t ZnTPP.

Por.	E_{cg} (eV)	I_{Ox}	I_{Red}	ΔE*(eV)			$\delta\epsilon_j$ (eV)	$\delta\epsilon_i$ (eV)	$\delta\epsilon_k$ (eV)
				ΔE_{cg}	ΔI_{Ox}	ΔI_{Red}			
ZnTPP	2.54	0.84	-1.36	-	-	-	-	-	-
1a	2.47	0.88	-1.13	-0.07	0.04	0.23	-0.04	-0.30	-0.23
2a	2.55	0.84	-1.40	0.01	0.00	-0.04	0	0.06	0.04
3a	2.51	0.84	-1.28	-0.03	0.00	0.08	0	-0.10	-0.08
4a	2.45	0.94	-1.17	-0.09	0.10	0.19	-0.10	-0.11	-0.19
5a	2.45	0.86	-1.11	-0.09	0.02	0.25	-0.02	-0.30	-0.25

Table S6. Modulation of frontier and subfrontier orbitals of $CoTPP(X)Y_2$ w.r.t CoTPP.

Por.	E_{cg} (eV)	I_{Ox}	I_{Red}	ΔE*(eV)			$\delta\epsilon_j$ (eV)	$\delta\epsilon_i$ (eV)	$\delta\epsilon_k$ (eV)
				ΔE_{cg}	ΔI_{Ox}	ΔI_{Red}			
CoTPP	2.69	1.06	-1.38	-	-	-	-	-	-
1c	2.54	1.14	-1.16	-0.14	0.08	0.22	-0.08	-0.09	-0.22
2c	2.69	1.11	-1.34	0.00	0.05	0.05	-0.05	-0.05	-0.05
3c	2.65	1.18	-1.05	-0.04	0.17	0.33	-0.12	-0.47	-0.33
4c	2.50	1.17	-0.99	-0.19	0.11	0.39	-0.11	-0.30	-0.39
5c	2.50	1.07	-1.13	-0.19	0.01	0.25	-0.01	-0.12	-0.25

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