Electronic Supplementary Information

Solventless mechanochemical metallation of porphyrins

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1. Experimental

Equipment used

Retsch Mixer mill (MM400) with a 25 ml stainless steel jar equipped with a 15 mm stainless steel ball. Bruker Avance 300 MHz NMR spectrometer. Perkin Elmer Lambda 25 UV-Vis spectrometer. Perkin Elmer Spectrum One FT-IR spectrometer

Materials

Materials were obtained from Sigma Aldrich and used as received.

Metallation of the porphyrin

In a typical experiment, a 25 ml stainless steel jar was charged with 25.3 mg or 151.5 mg of *meso*-tetraphenylporphyrin and the required amount of metal acetate salt (see Tables S1 and S2) and milled for 20-90 min at 25-30 Hz in a shaker mill.

Table S1 Quantities of materials used to prepare metallated porphyrins (small scale)

Complex	Metal salt	Purity of metal salt (%)	Moles	Quantity (mg)
H_2TPP	/	99	$4.07x10^{-5}$	25.3
ZnTPP	$Zn(OAc)_2.2H_2O$	99.99	$4.07x10^{-5}$	8.9
NiTPP	$Ni(OAc)_2.4H_2O$	98	$4.07x10^{-5}$	10
CuTPP	$Cu(OAc)_2.H_2O$	99.99	$4.07x10^{-5}$	7.4
FeTPP	$Fe(OAc)_2$	99.99	$4.07x10^{-5}$	7.1

Table S2 Quantities of materials used to prepare metallated porphyrins (large scale)

Complex	Metal salt	Purity of metal salt (%)	Moles	Quantity (mg)
H_2TPP	/	99	$2.44x10^{-4}$	151.5
ZnTPP	$Zn(OAc)_2.2H_2O$	99.99	$2.44x10^{-4}$	54
NiTPP	$Ni(OAc)_2.4H_2O$	98	$2.44x10^{-4}$	62
CuTPP	$Cu(OAc)_2.H_2O$	99.99	$2.44x10^{-4}$	44

2. Analytical data for the metallated porphyrins

Table S3 UV visible data for porphyrins (dichloromethane solution)

Porphyrin	Soret Bands	Q bands
$TPPH_2$	418	516, 550, 590, 645
ZnTPP	418	547, 584
NiTPP	417	526
CuTPP	416	540, 620
FeTPP	417	509, 580

Table S4 IR data for porphyrins (KBr disc)

Porphyrin	IR Spectroscopic Data
$TPPH_2$	3317, 1594, 983, 800
ZnTPP	1599, 1002, 797
NiTPP	1599, 1007, 797
CuTPP	1603, 1006, 801
FeTPP	1599, 1007, 802

Table S5 Mass spectrometric data for porphyrins

Porphyrin	Ion observed (M+ calc.)
ZnTPP	677.17 (678.11)
NiTPP	671.18 (671.41)
CuTPP	676.16 (676.26)
FeTPP	669.17 (668.56)

Table S6 ^1H NMR data for porphyrins ($CDCl_3$)

Porphyrin	Chemical shift / ppm				
	Proton				
	Pyrrole	Ortho	Meta	Para	N-H
$TPPH_2$	8.85	8.23	7.77	7.77	-2.79
ZnTPP	8.74	8.02	7.69	7.69	-
NiTPP	8.74	8.02	7.69	7.69	-

3. Spectra

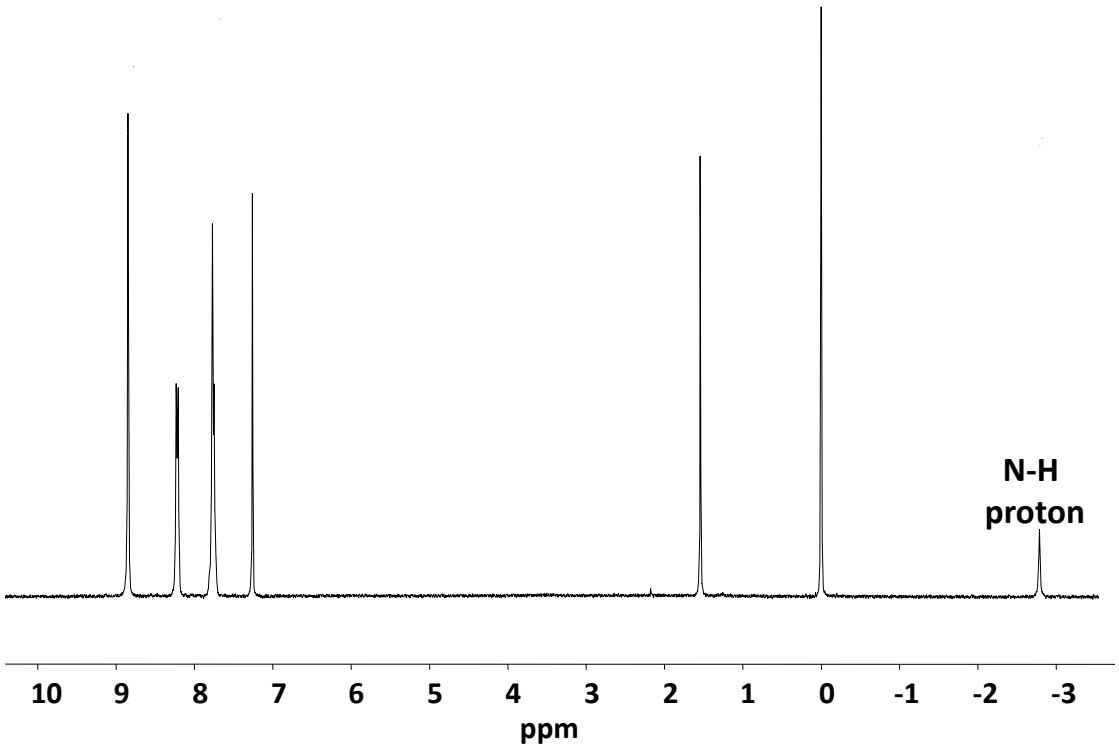

Figure S1 ^{1}H-NMR spectrum of H_2TPP

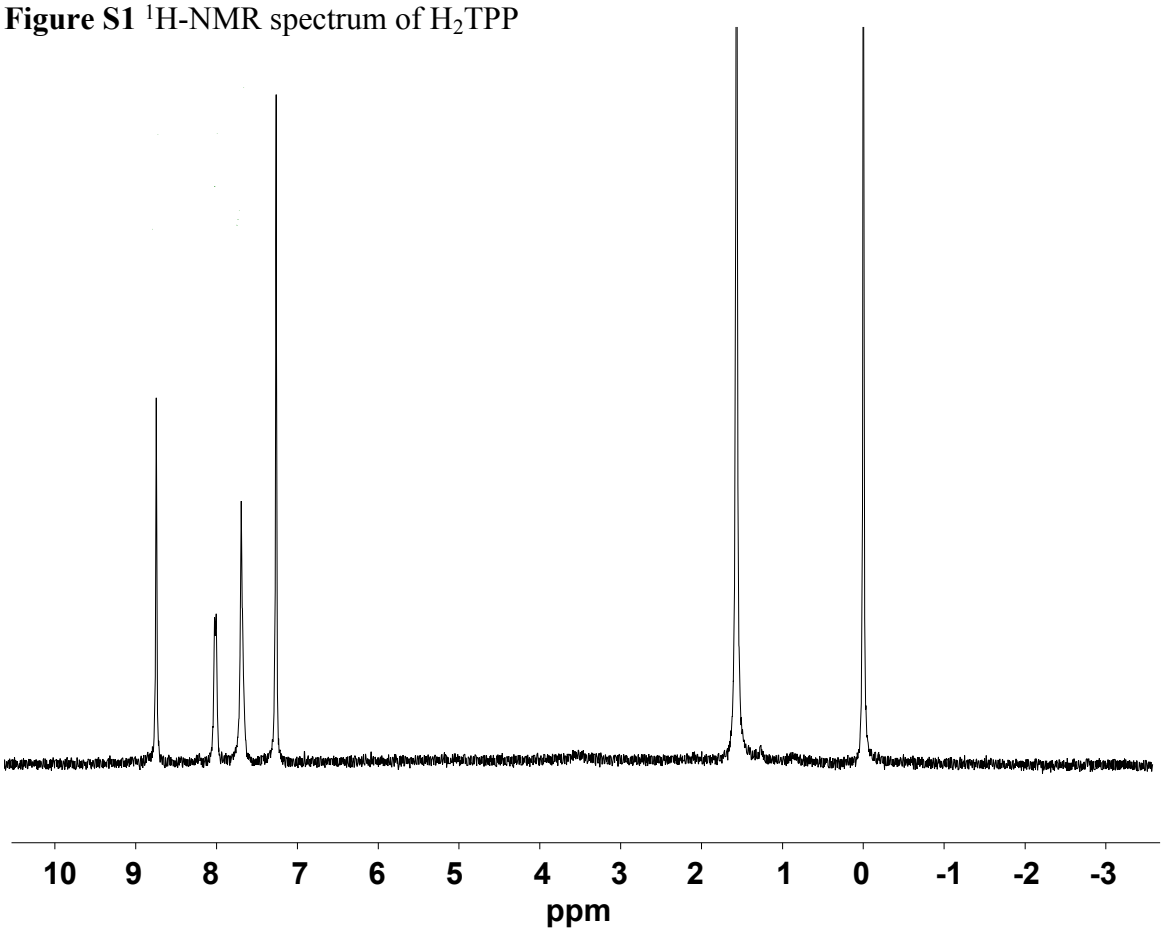

Figure S2 ^{1}H-NMR spectrum of ZnTPP

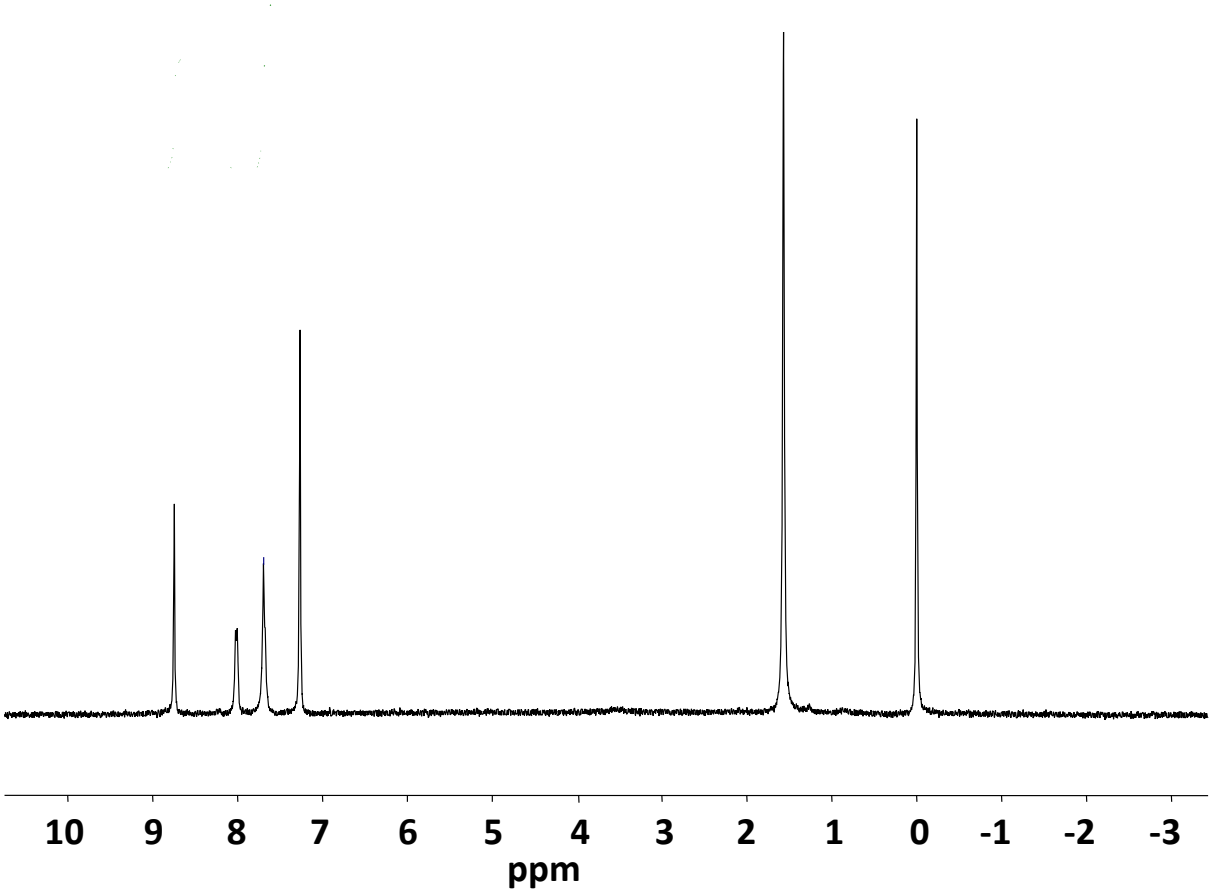

Figure S3 ^{1}H-NMR spectrum of NiTPP

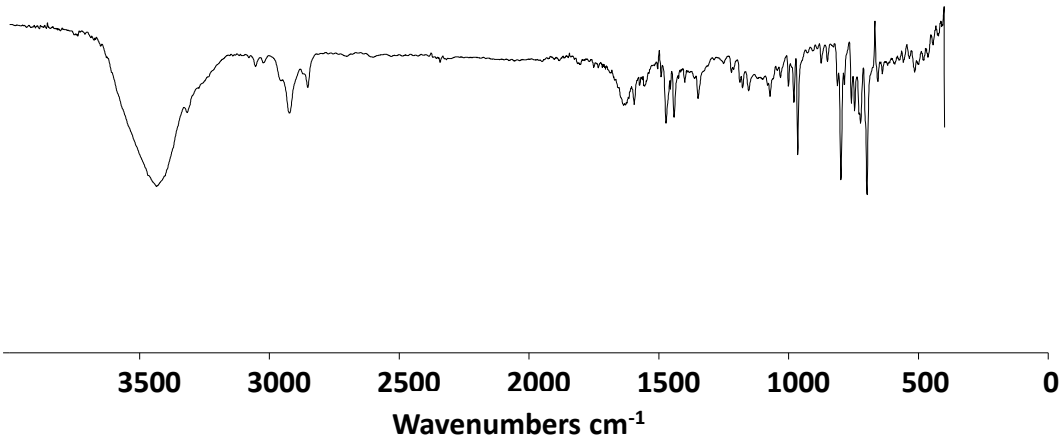

Figure S4 FT-IR spectrum of H_2TPP

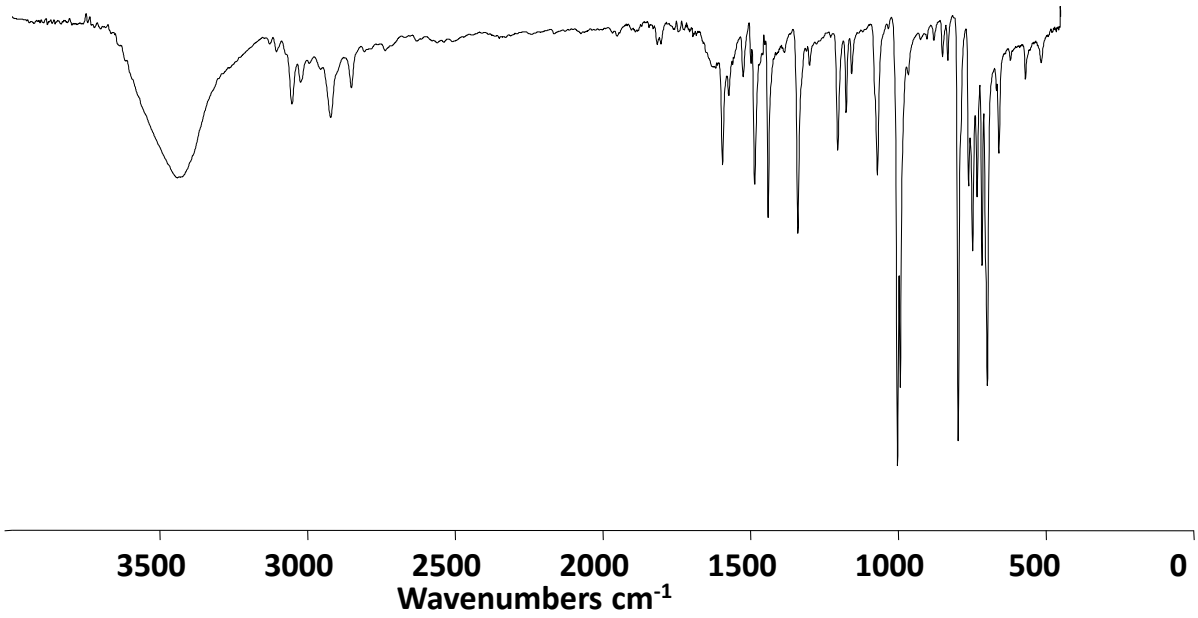

Figure S5 FT-IR spectrum of ZnTPP

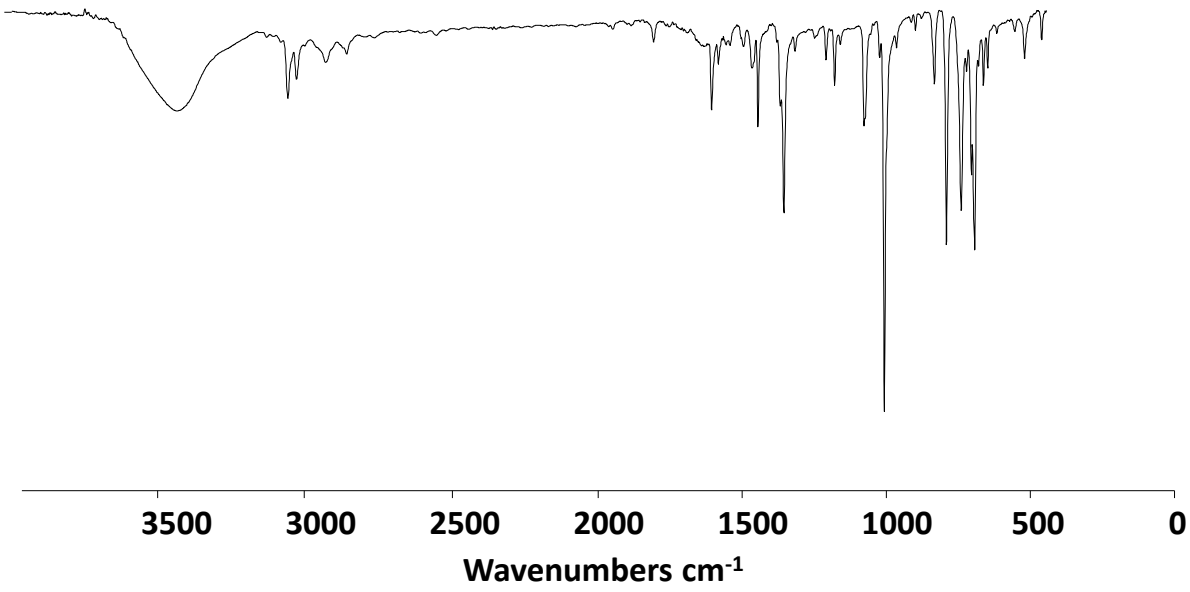

Figure S6 FT-IR spectrum of NiTPP

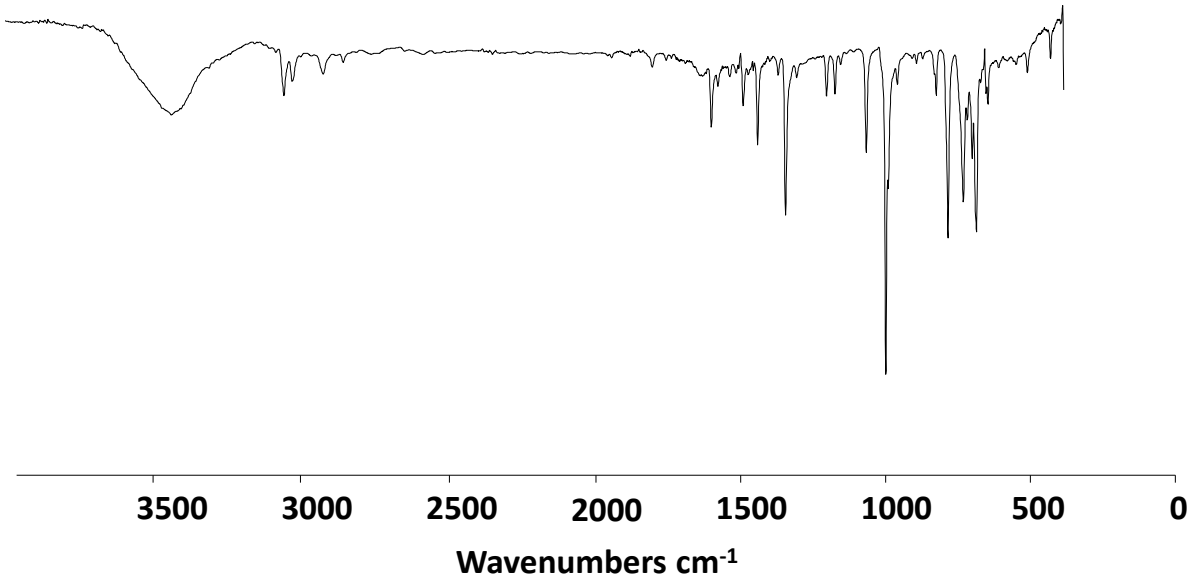

Figure S7 FT-IR spectrum of CuTPP

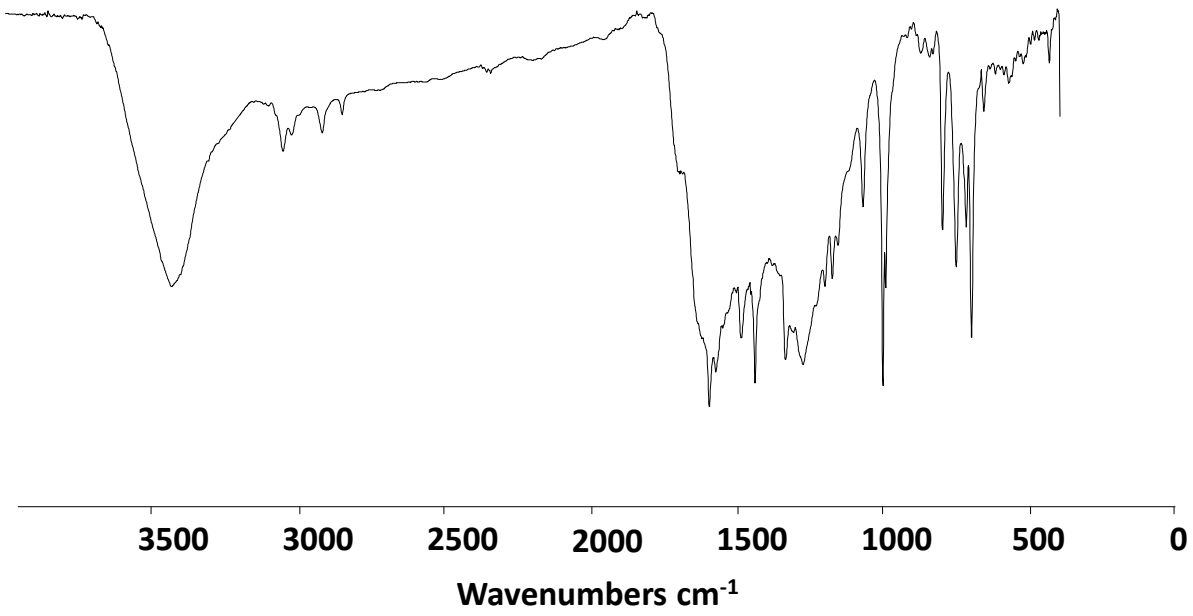

Figure S8 FT-IR spectrum of FeTPP

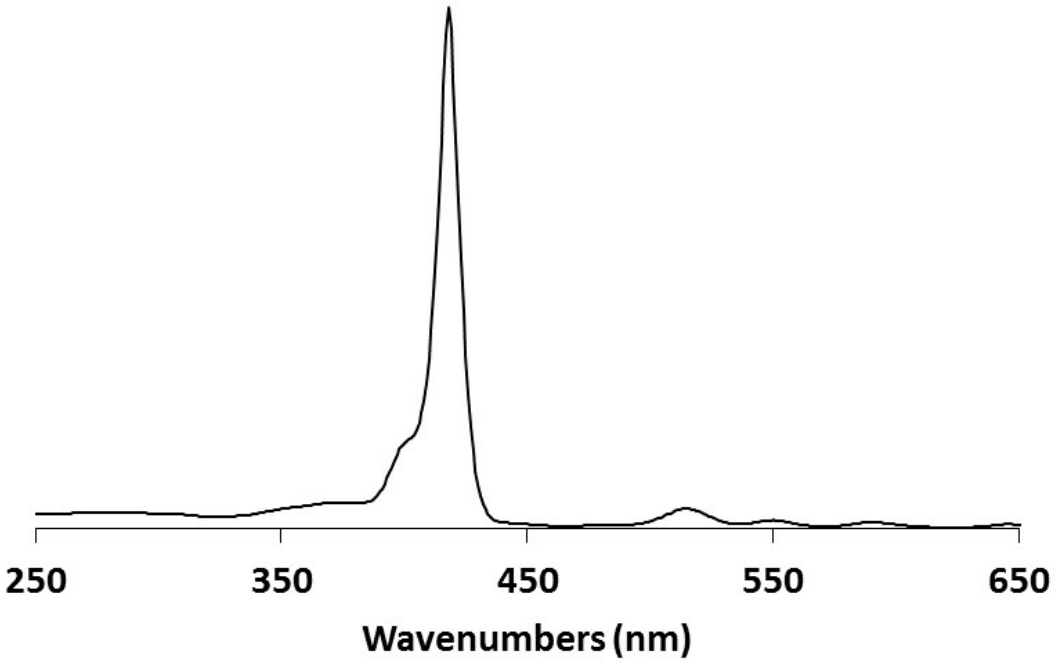

Figure S9 Absorption spectrum of $TPPH_2$ showing the Soret and Q bands.

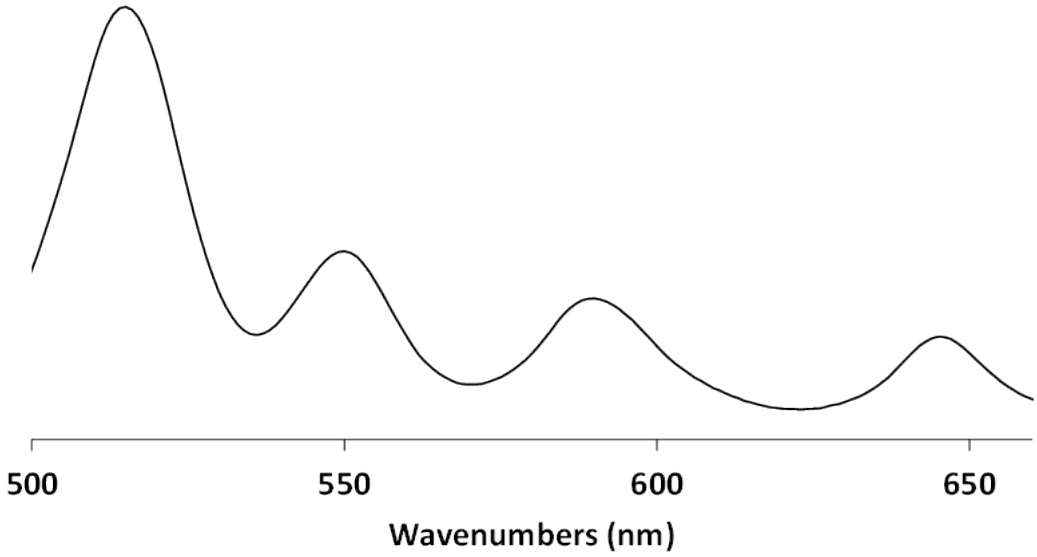

Figure S10 Absorption spectrum of $TPPH_2$ showing the Q bands.

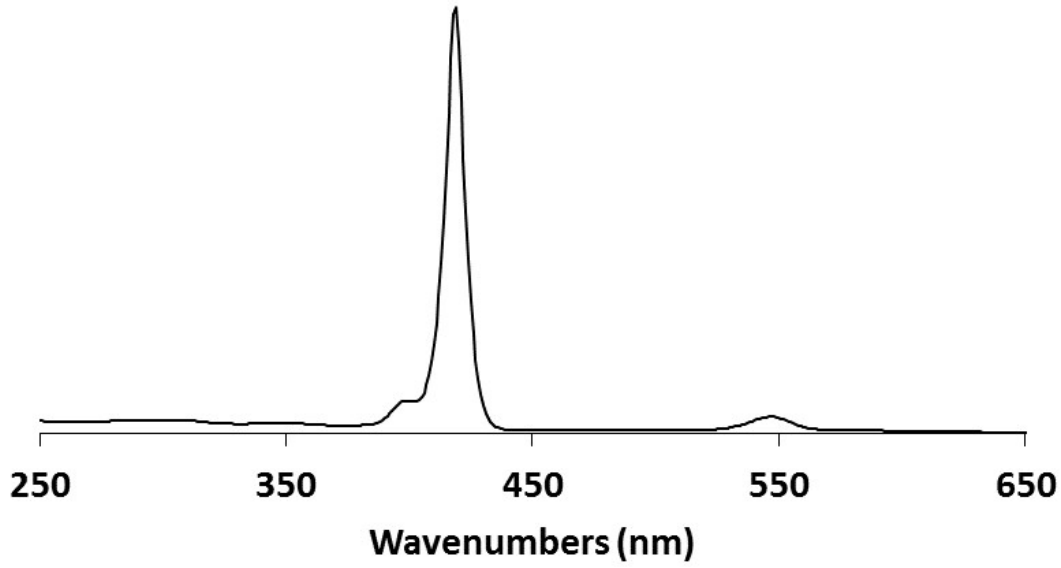

Figure S11 Absorption spectrum of ZnTPP showing the Soret and Q bands.

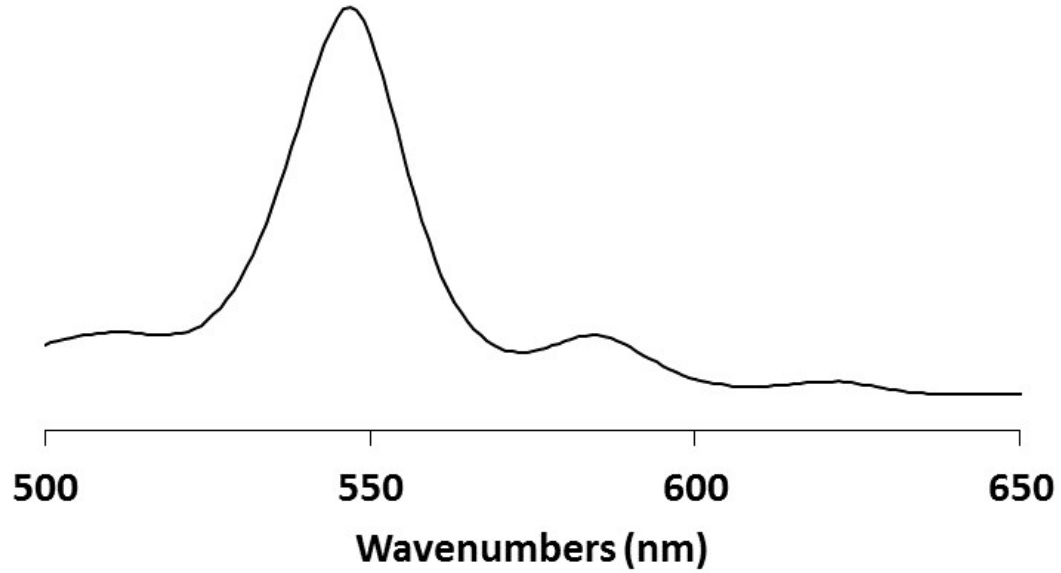

Figure S12 Absorption spectrum of ZnTPP showing the Q bands.

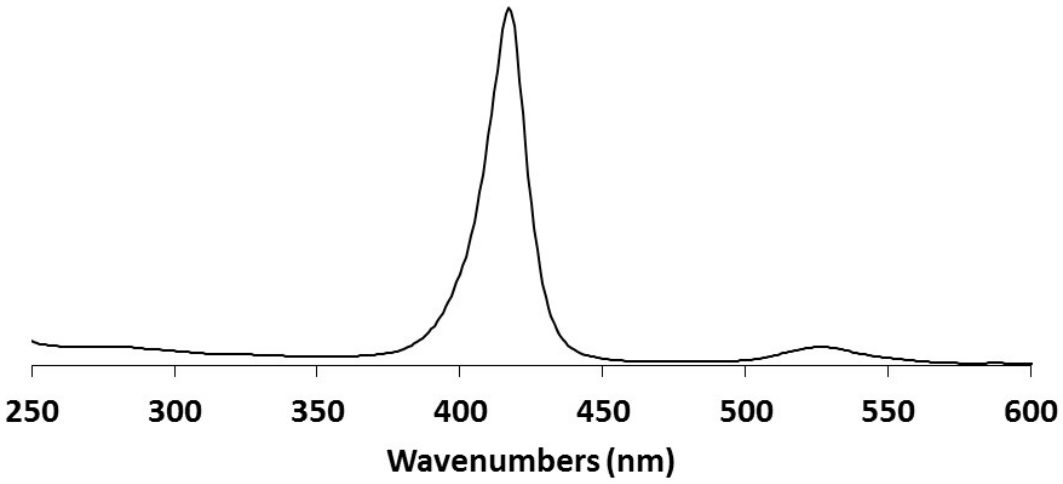

Figure S13 Absorption spectrum of NiTPP showing the Soret and Q bands

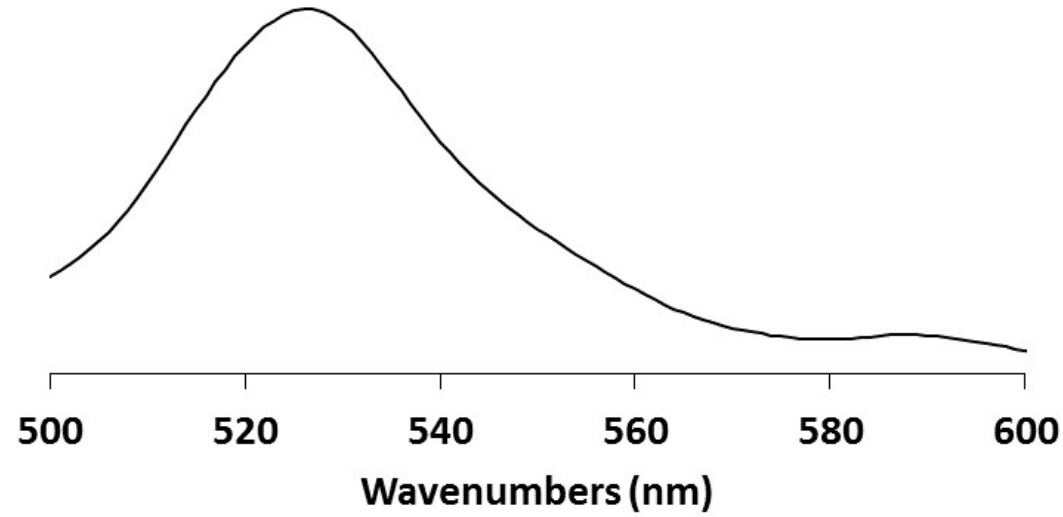

Figure S14 Absorption spectrum of NiTPP showing the Q bands

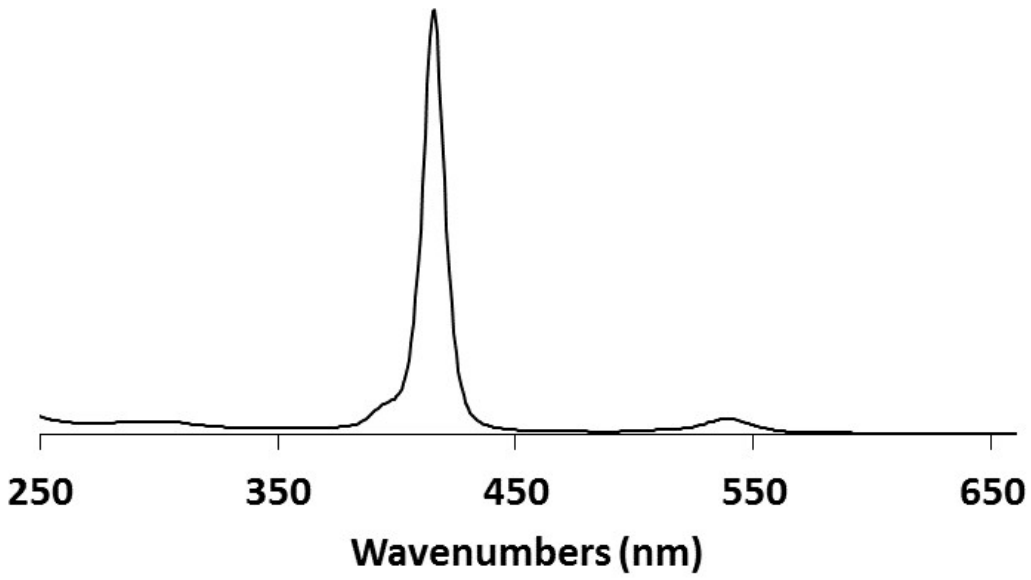

Figure S15 Absorption spectrum of CuTPP showing the Soret and Q bands

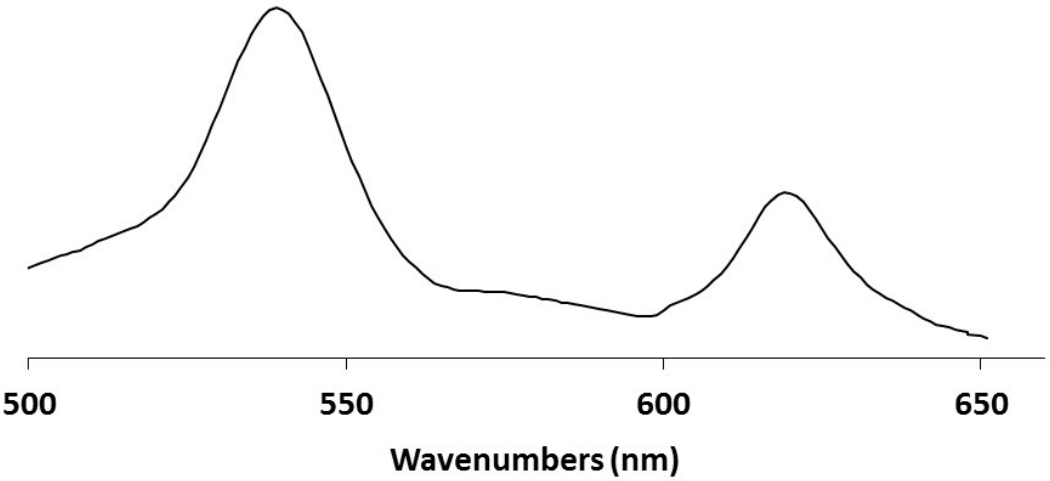

Figure S16 Absorption spectrum of CuTPP showing the Q bands

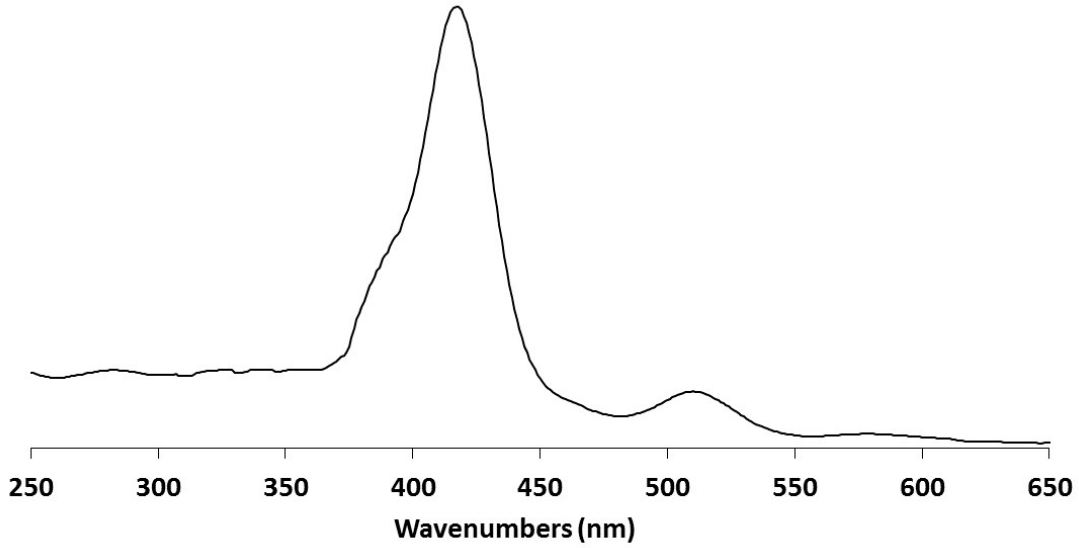

Figure S17 Absorption spectrum of FeTPP showing the Soret and Q bands

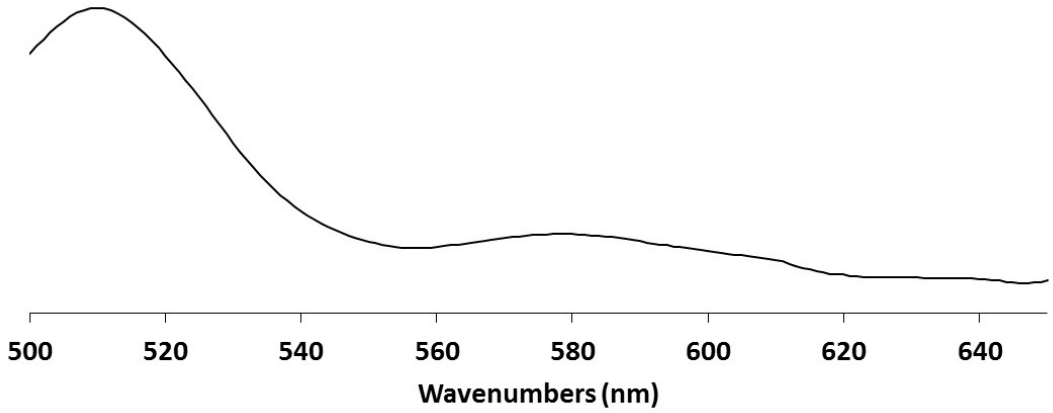

Figure S18 Absorption spectrum of FeTPP showing the Q bands

Table S7 Summary of unsuccessful attempted metalation reactions with Au, Mg, Ag, Pt, Li, Mn and Co

Metal	Metal salt	Speed (Hz)	Time (Min)	Additives (cm^3)	Successful (Y/N)
Gold	$Au(OAc)_3$	25	20	/	N
		25	60	/	N
		25	60	Py (0.2)	N
		30	90		N
		30	90	DMF (0.4)	N
Magnesium	$Mg(OAc)_2.4H_2O$	25	40	/	N
		25	40	DMF (0.2)	N
		25	60	/	N
		25	80	/	N
		25	100	/	N
		25	100	DMF (0.2)	N
		25	270	/	N
		30	30	/	N
		30	30	DMF (0.2)	N
		30	30	DMF (0.4)	N
		30	40	/	N
		30	40	/	N
		30	120	DMF (0.2)	N
		30	180	/	N
		30	180	DMF (0.2)	N
Silver	Ag(OAc)	25	20	/	N
		25	60	/	N
		30	30	/	N
		30	45	/	N
		30	120	/	N
		30	30	MeOH (0.6)	N
		30	30	Py (0.4)	N
		30	30	H_2O (0.4)	N
		30	30	MeOH (0.4)	N
		30	45	MeOH (0.4)	N
		30	60	/	N
		30	60	MeOH (0.4)	N
		30	90	MeOH (0.4)	N
		30	120	MeOH (0.4)	N
		30	180	MeOH (0.4)	N

Platinum	PtO_2	25	40	/	N
	$H_2Pt(OH)_6$	25	40	/	N
Lithium	Li(OAc)	25	20	/	N
		25	40	/	N
Manganese	$Mn(OAc)_2.4H_2O$	25	20	/	N
		25	40	/	N
Cobalt	$Co(OAc)_2$	25	20	/	N
		25	60	/	N