Formation of Unusual Dithiaphlorins from Condensation of 2,5-Bis(arylhydroxymethyl)thiophene and Pyrrole

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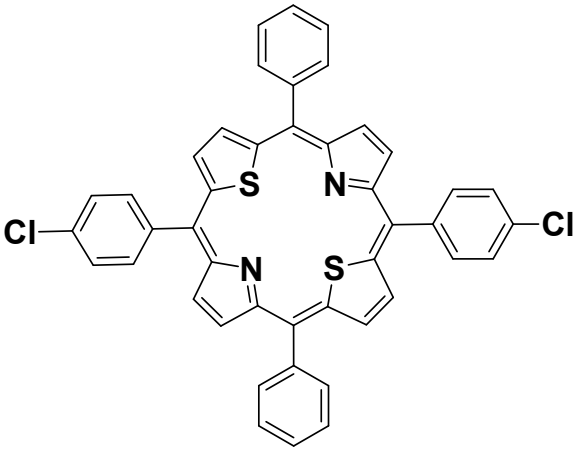
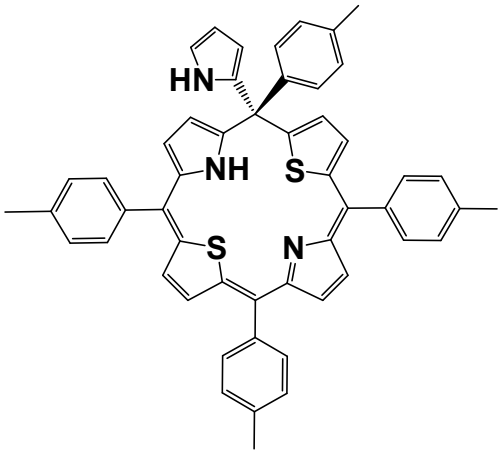


Chart S1: Molecular structure of 5,10-bis(*p*-chlorophenyl)-10,20-bisphenyl-21,23-dithiaporphyrin **(4a)**.



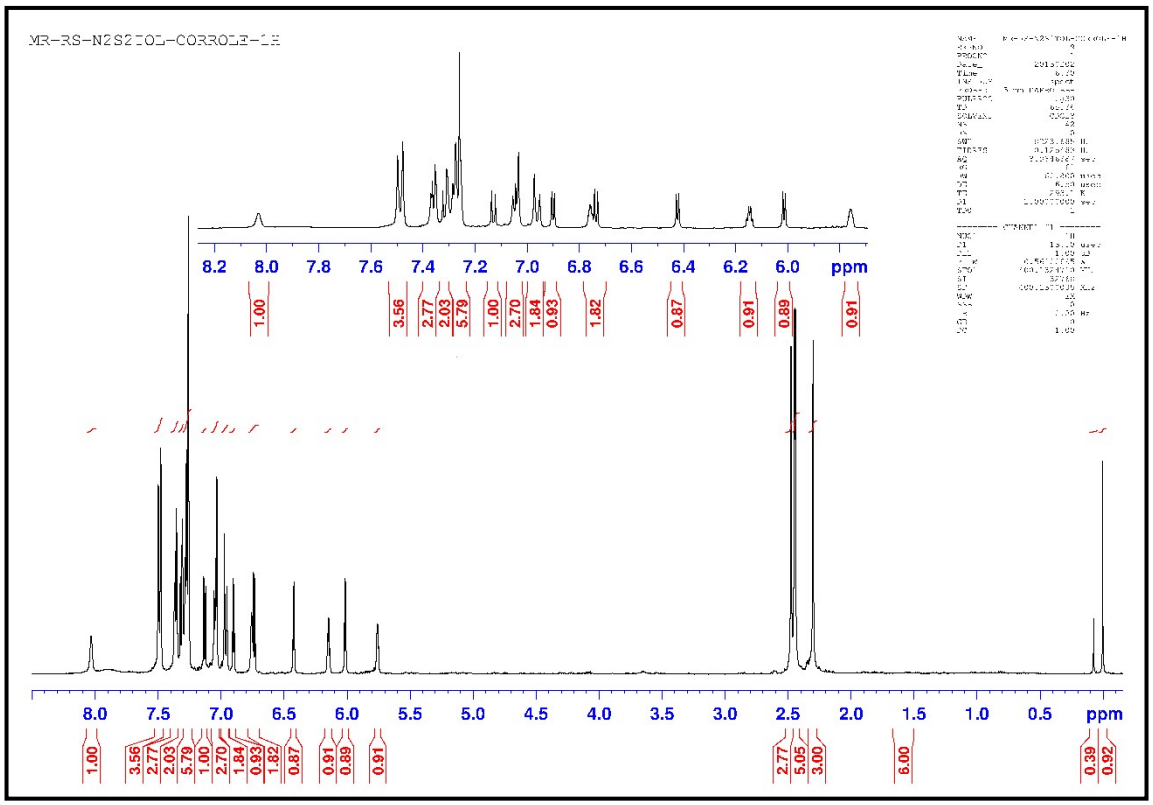
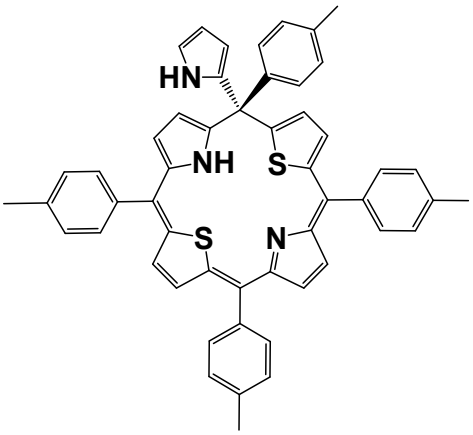


Figure S1: ^{1}H NMR Spectrum of compound **1a**.



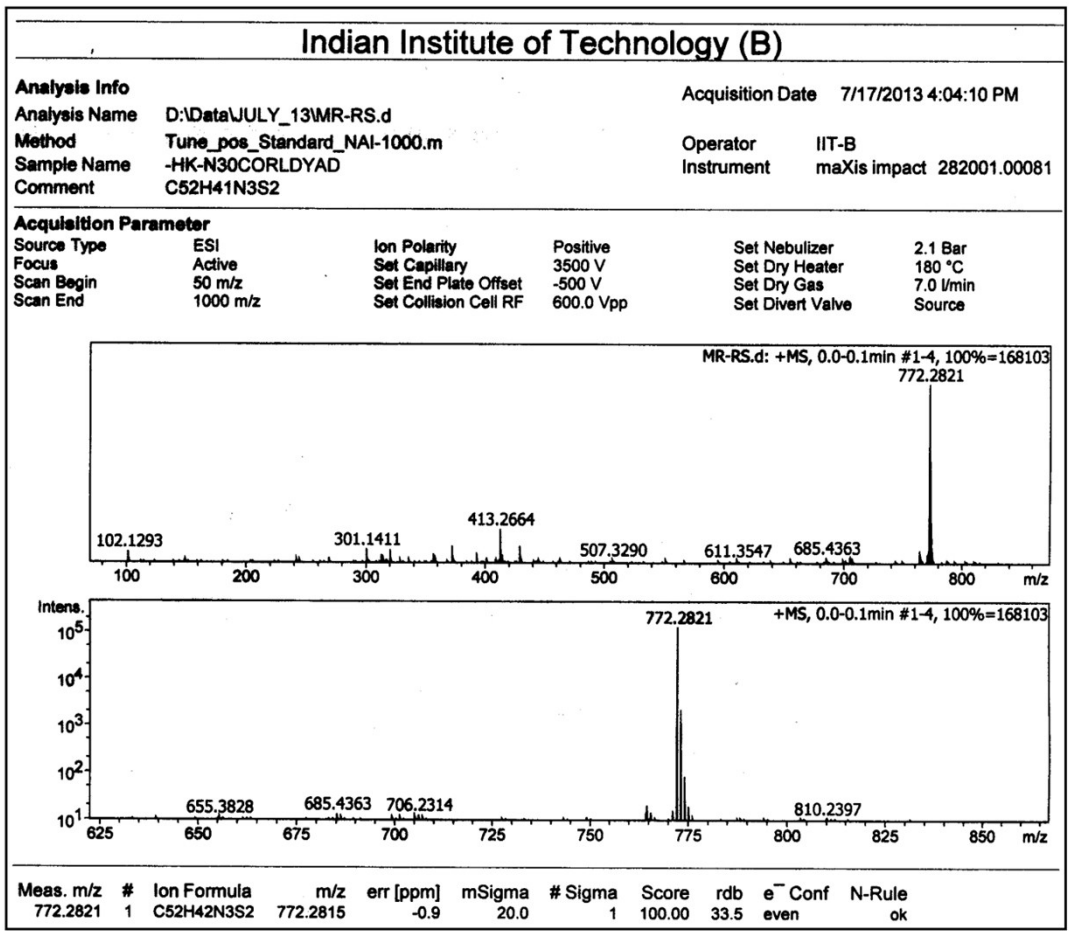


Figure S2: HRMS of compound **1a**.

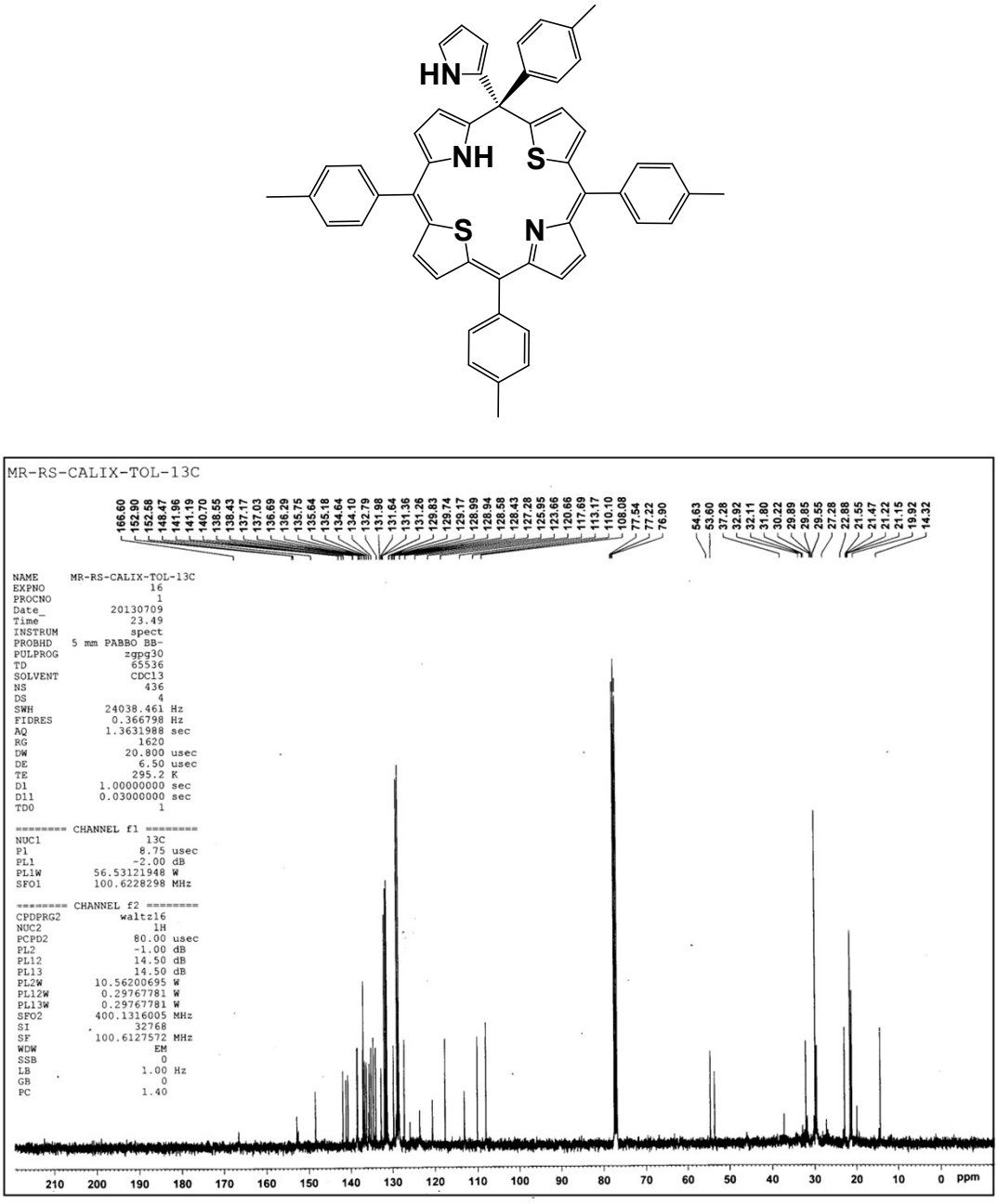
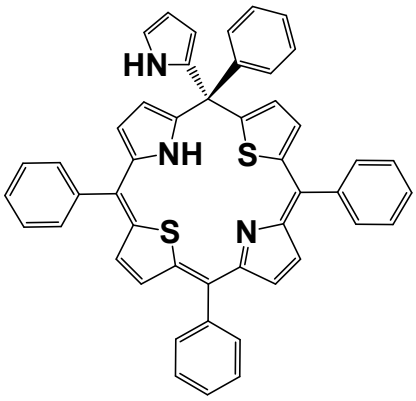


Figure S3: ^{13}C NMR spectrum of compound **1a** recorded in $CDCl_3$.



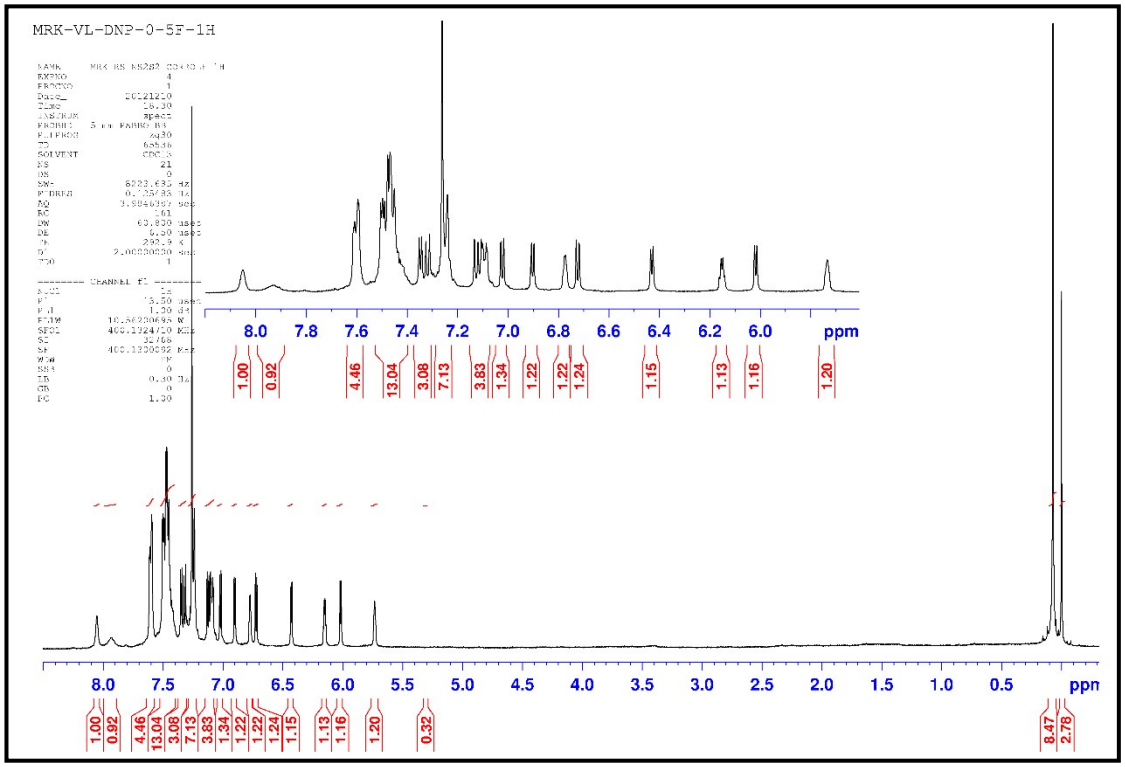
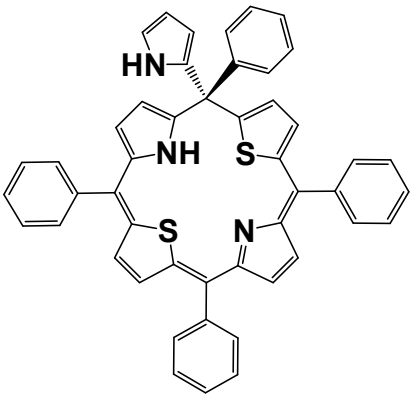


Figure S4: ^{1}H NMR Spectrum of compound **2a**.



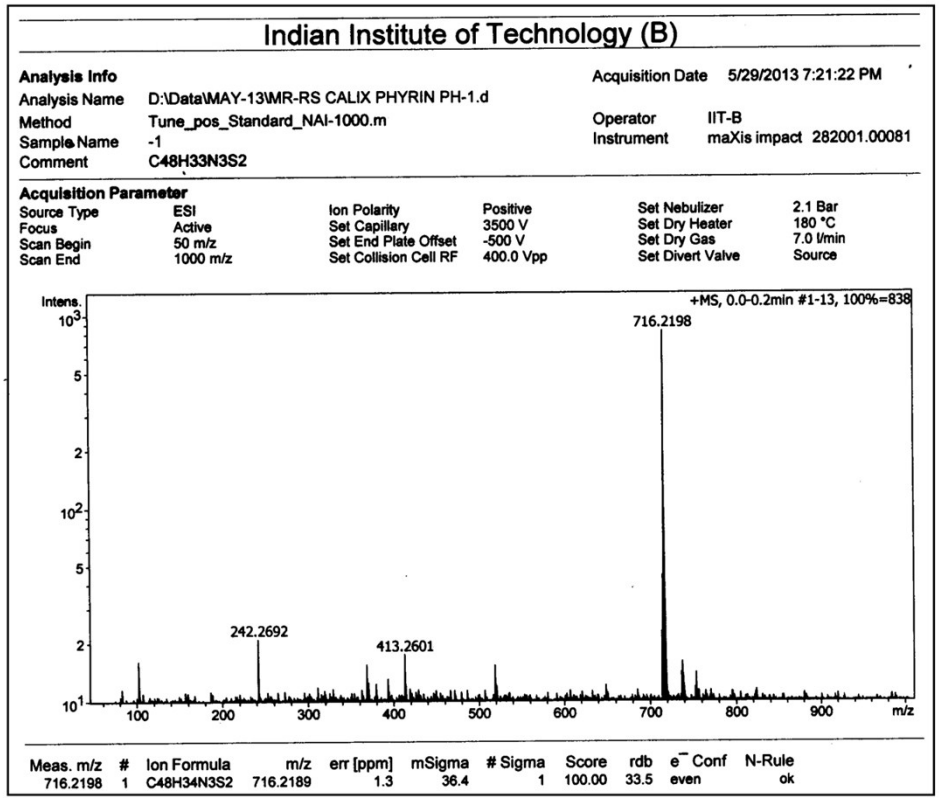
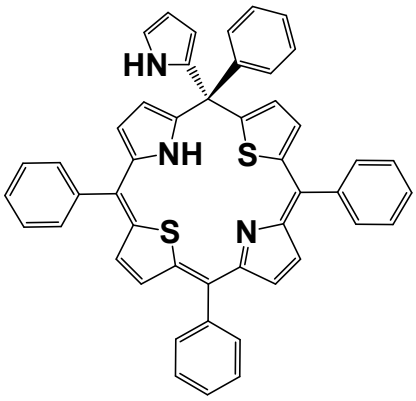


Figure S5: HRMS of compound **2a**.



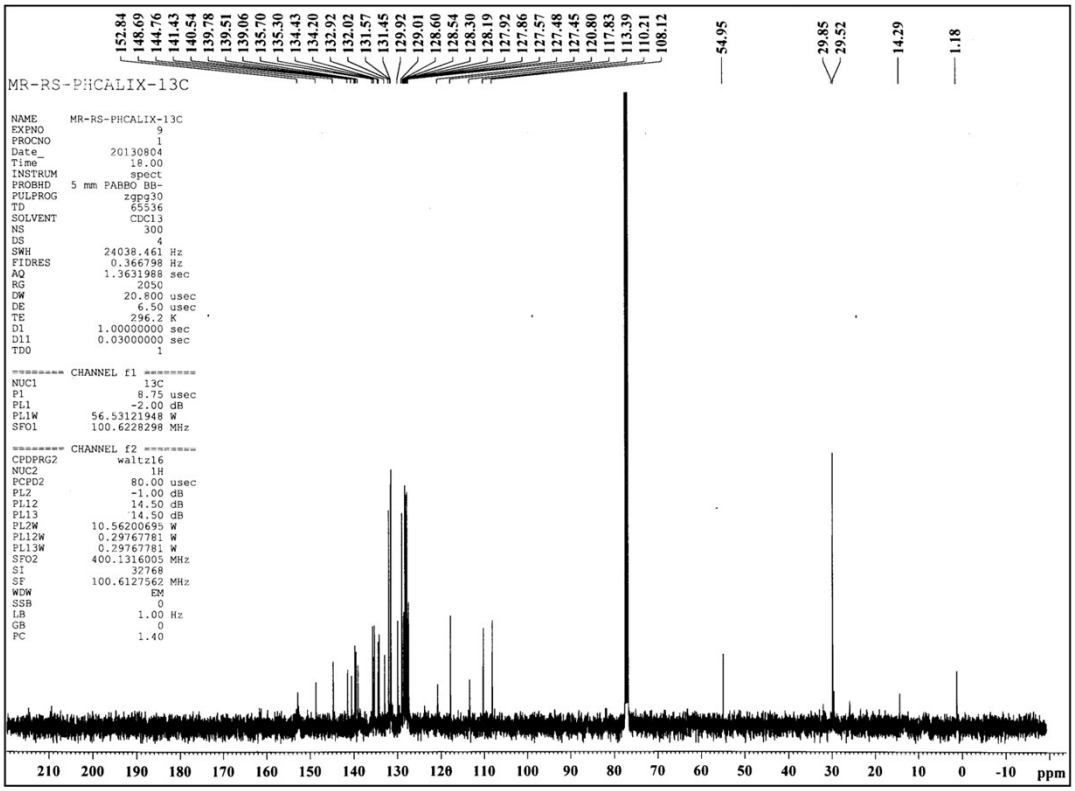


Figure S6: ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$.

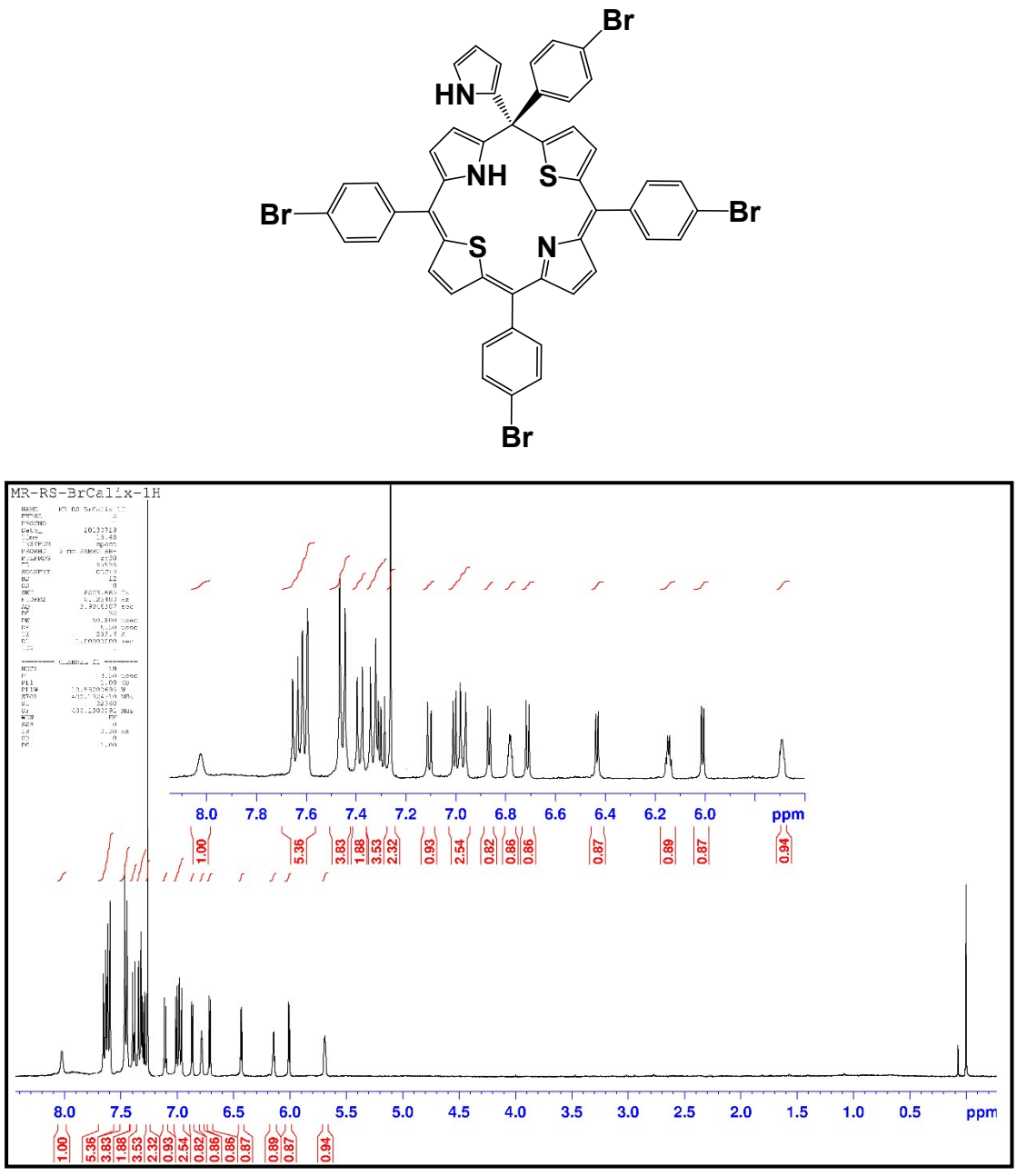
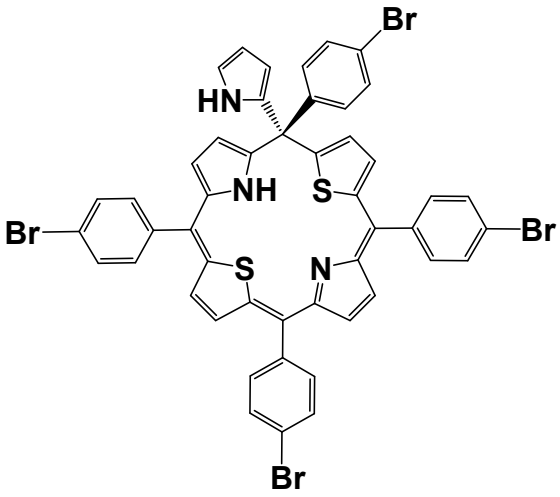


Figure S7: ^{1}H NMR spectrum of compound **3a** recorded in $CDCl_3$.



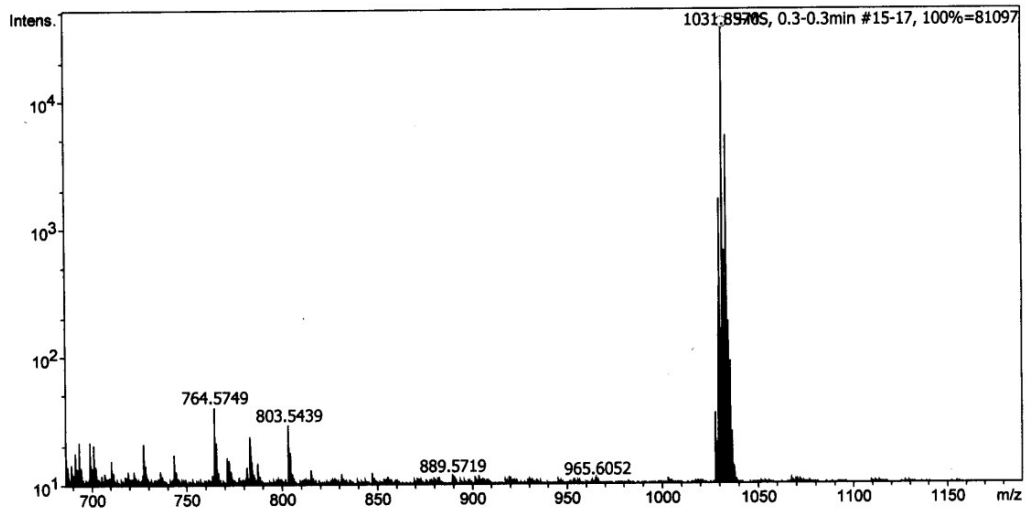
Indian Institute of Technology (B)

Analysis Info

Analysis Name	D:\Data\JULY_13\MR-RS-BR-CALIX.d	Acquisition Date	7/17/2013 3:23:05 PM
Method	Tune_pos_Standard_NAI-1500.m	Operator	IIT-B
Sample Name	MR-RS-BR-CALIX	Instrument	maXis impact 282001.00081
Comment	C48H29BR4N3S2		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.1 Bar
Focus	Active	Set Capillary	3200 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	7.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	900.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
1031.8570	1	C47H30Br4N3OS2	1031.8558	1.1	444.5	1	100.00	32.5	even	ok

Figure S8: HRMS of compound **3a**.

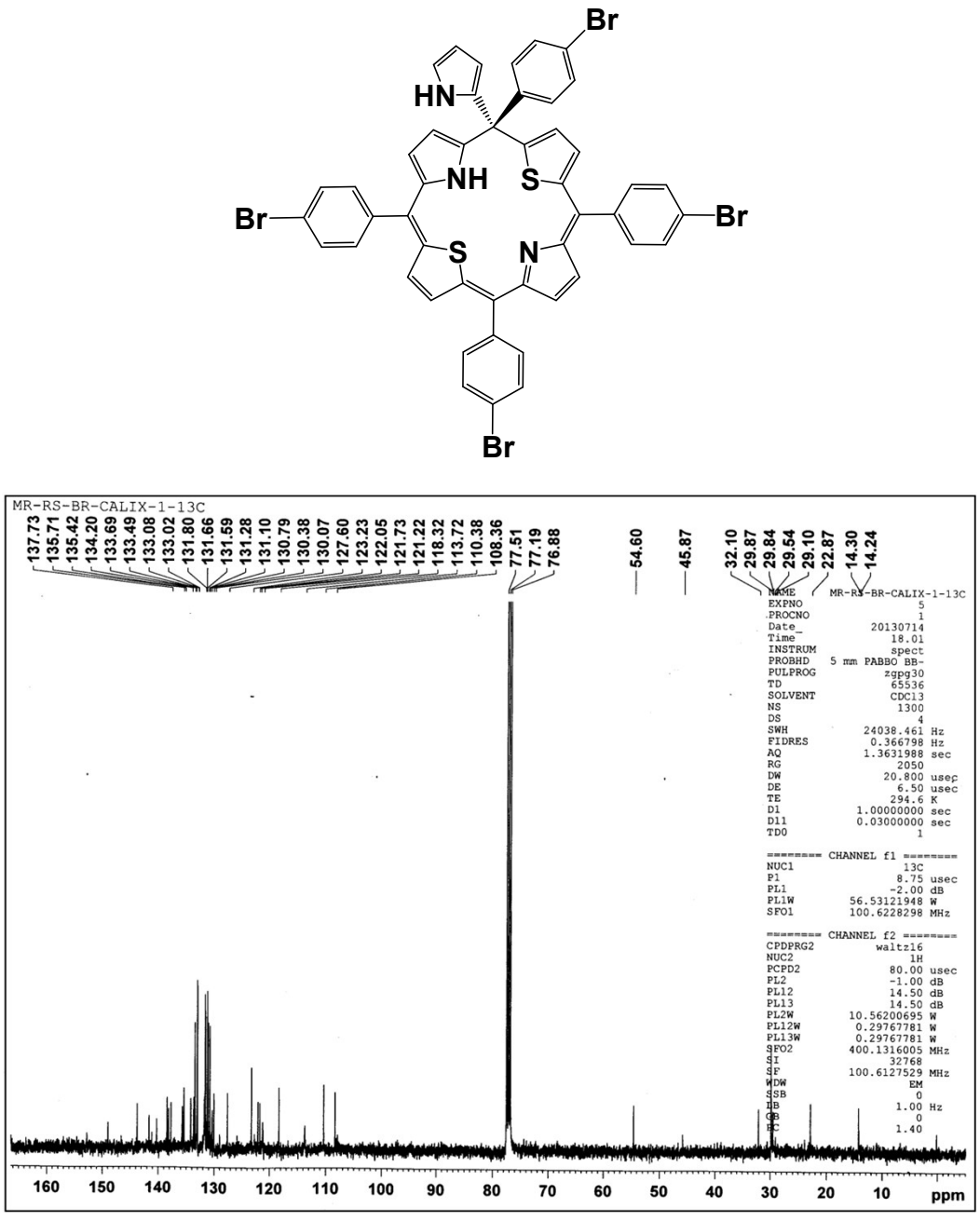


Figure S9: ^{13}C NMR spectrum of compound **3a** recorded in $CDCl_3$.

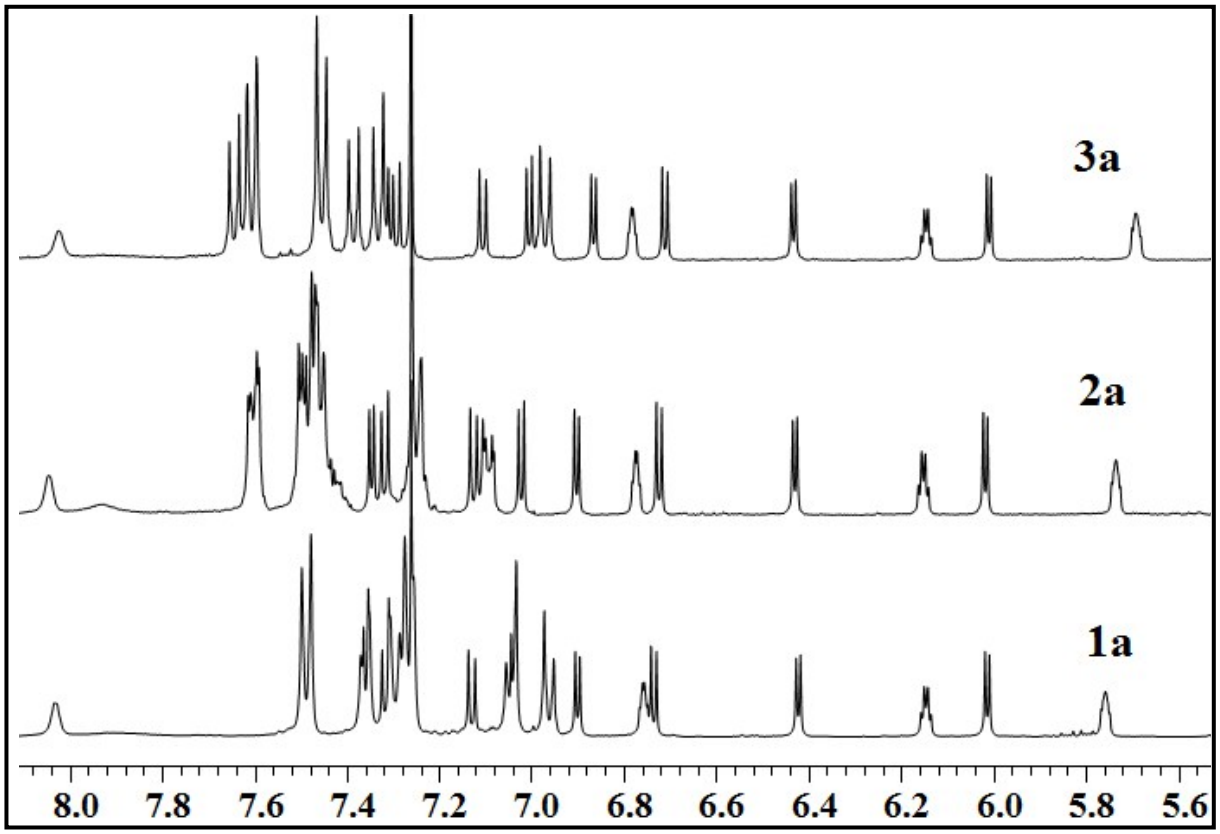


Figure S10: Partial ^{1}H NMR overlay of compound **1a-3a** recorded in $CDCl_3$.

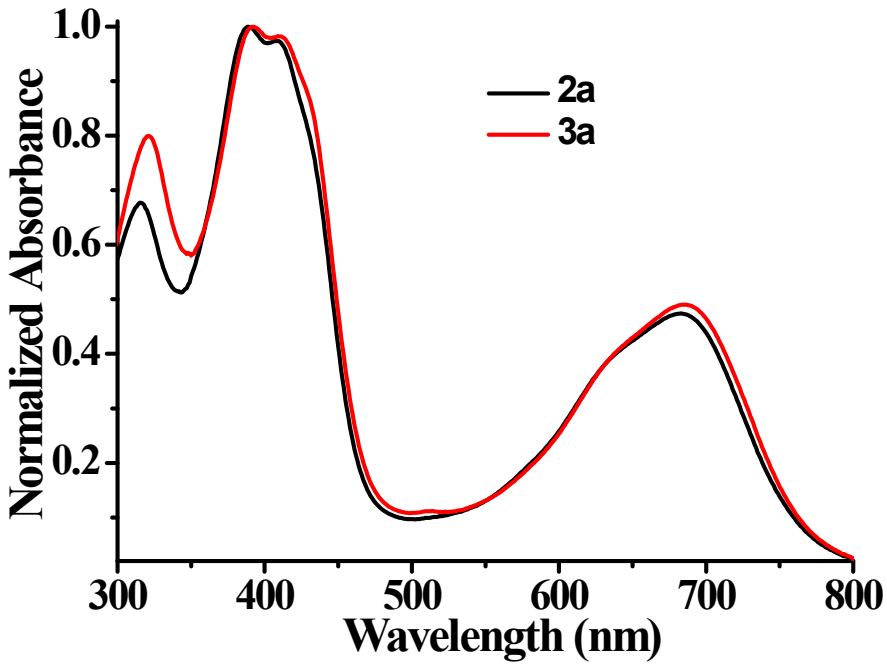


Figure S11: Normalized absorption spectra of compound **2a** and **3a** recorded in chloroform.

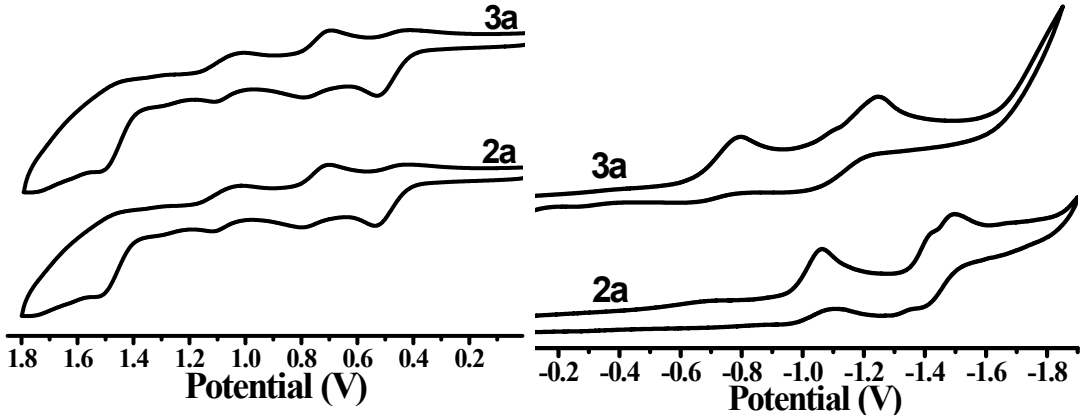


Figure S12: Redox waves of cyclic voltammograms of compound **2a** and **3a** recorded in CH_2Cl_2 solvent using tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte and the saturated calomel electrode (SCE) as a reference electrode at scan rates of 50 mV s^{-1}.

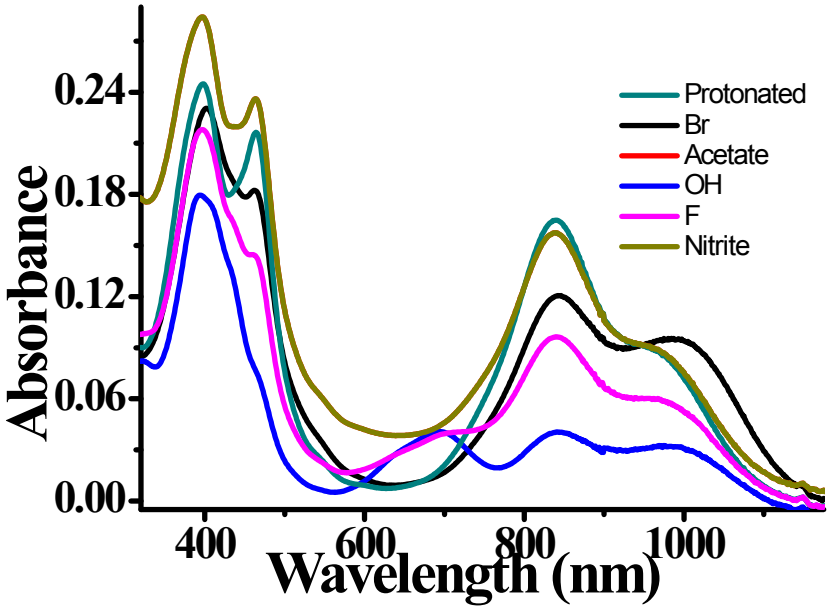


Figure S13: Absorption spectra of **1a.H**$^{+}$ upon addition of various anions.

Table S1: Crystal tata and data Collection Parameters for Compound **1a**.

Parameters	Compound **1a**
mol formula	$C_{52}H_{41}N_3S_2$
formula weight	772.00
crystal system	Orthorhombic,
space group	*Pbcn*
temp (K)	200 K
a (Å)	27.1164 (12) Å
b (Å)	14.8221 (7) Å
c (Å)	20.8971 (10) Å
α (deg)	90.00
β (deg)	90.00
γ (deg)	90.00
V ($Å^3$)	8399.0 (7)
Z	8
μ (mm^{-1})	0.17
dcalcd (Mg cm^{-3})	1.221
F(000)	3248
2θ range (deg)	25.1°-1.5°
independent reflection	7406
R1, WR2 [I> 2σ(I)]	0.1171, 0.2527
R1, WR2 (all data)	0.0826, 0.2335
GOF	1.10
largest diff. peak/hole, (e $Å^{-3}$)	0.69, -0.41