Supporting Information

Synthesis and Specific Fluoride Binding Properties of Expanded Dithiacalixphyrins

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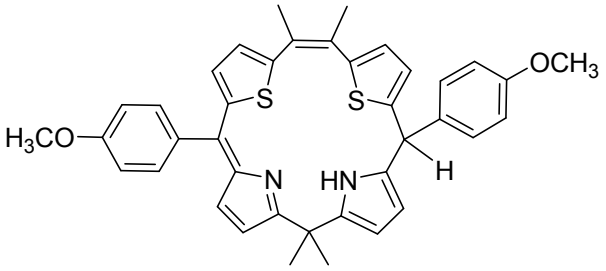


3a

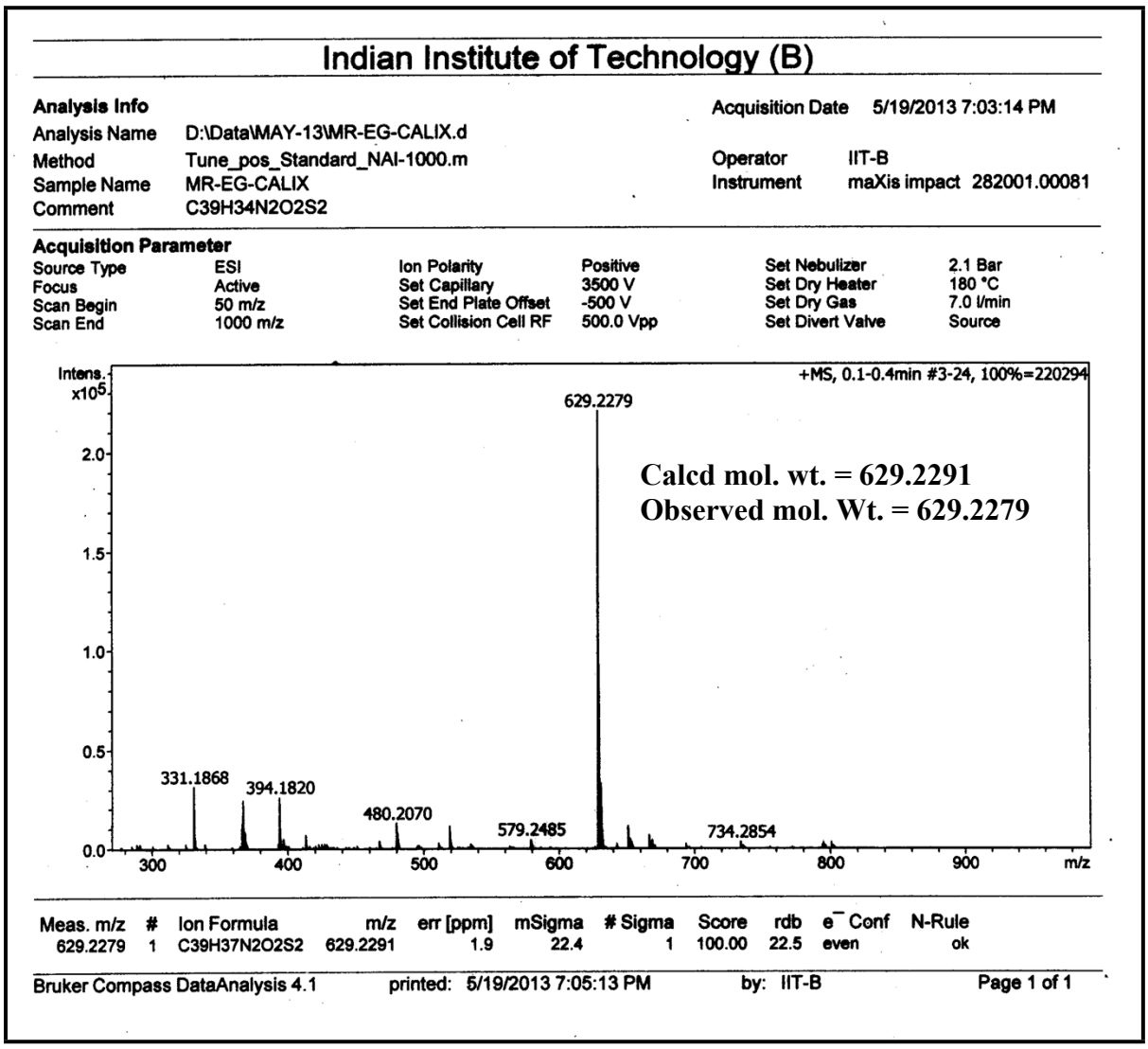
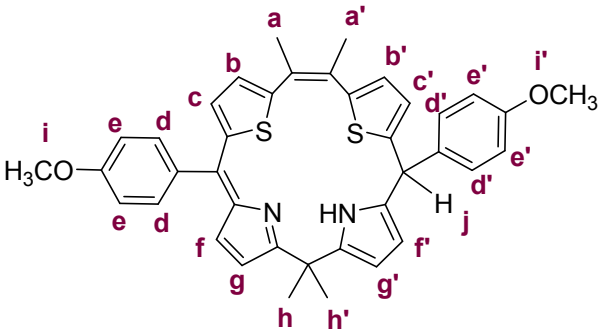


Figure S1: HRMS spectrum of compound **3a**


a
a'
b
b'
c
c'
d
d'
e
e'
i
i'
H_3CO
OCH_3
S
S
N
HN
H
j
f
f'
g
g'
h
h'

3a

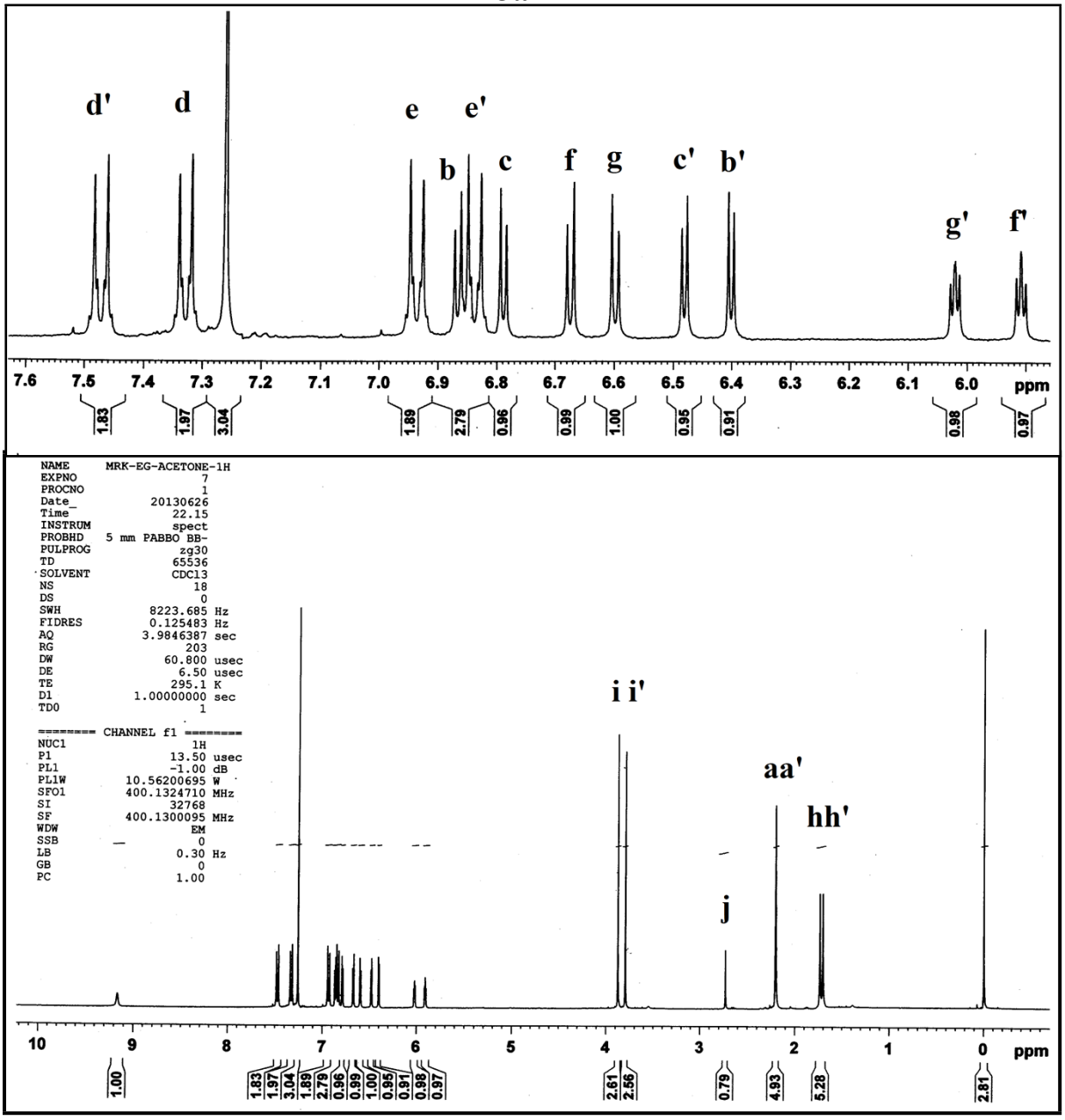
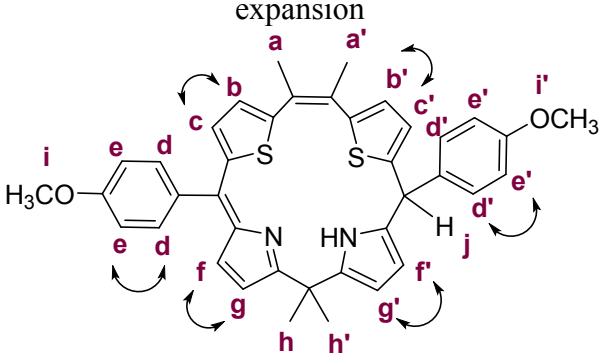

d'
d
e
e'
b
c
f
g
c'
b'
g'
f'
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
ppm
1.83
1.97
3.04
1.89
2.79
0.96
0.99
1.00
0.95
0.91
0.98
0.97
NAME MRK-EG-ACETONE-1H
EXPNO 7
PROCNO 1
Date_ 20130626
Time_ 22.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300095 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
i i'
aa'
hh'
j
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.83
1.97
3.04
1.89
2.79
0.96
0.99
1.00
0.95
0.91
0.98
0.97
2.61
2.56
0.79
4.93
5.28
2.81

Figure S2: ^{1}H NMR spectrum of compound **3a** recorded in $CDCl_3$. Above shows the expansion



3a

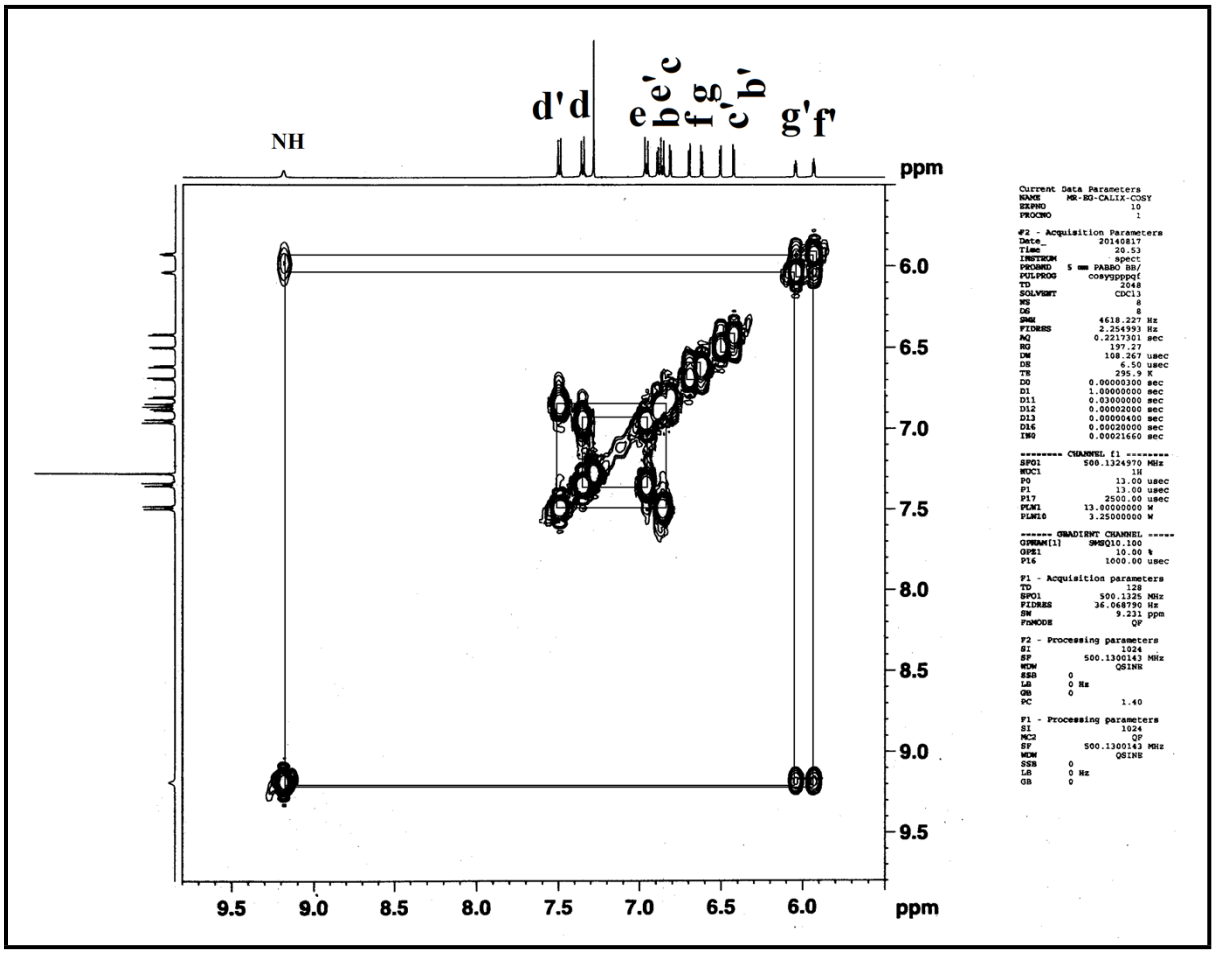


Figure S3: ^{1}H-^{1}H COSY spectrum of compound **3a** recorded in $CDCl_3$

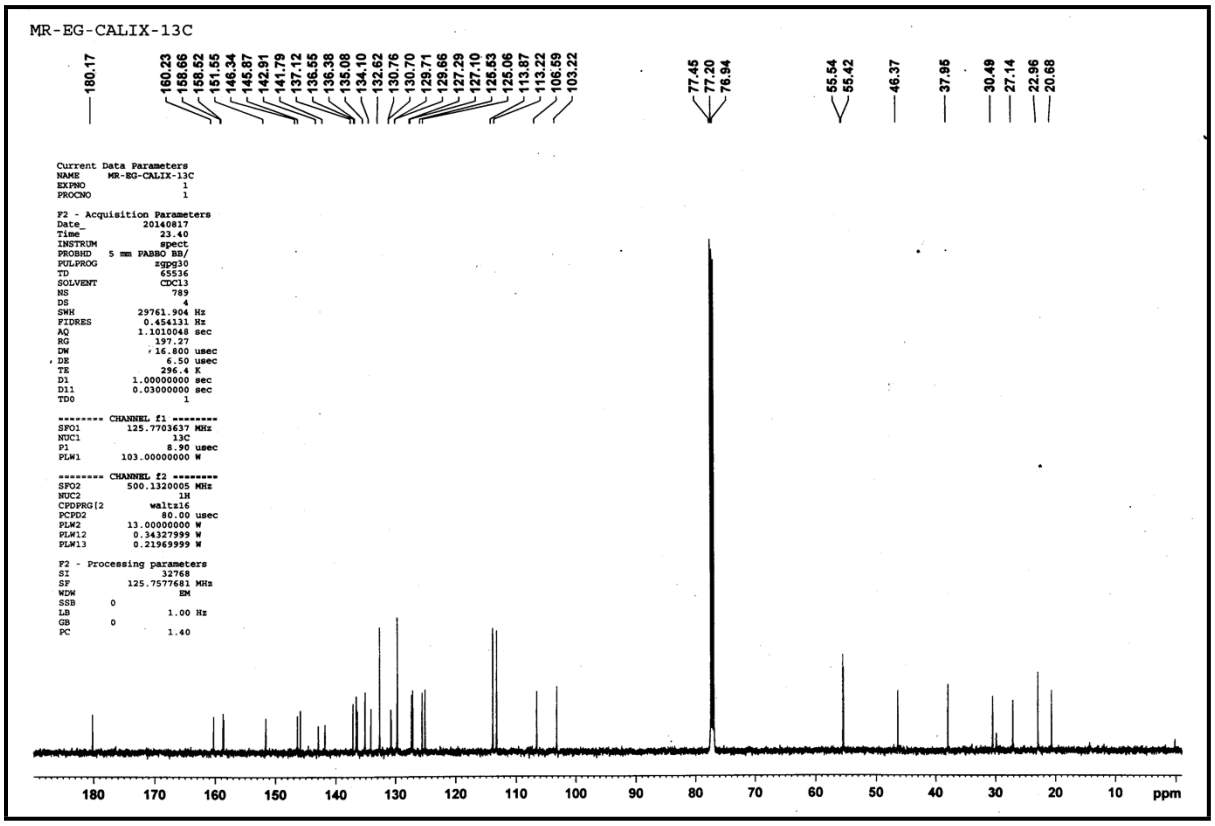
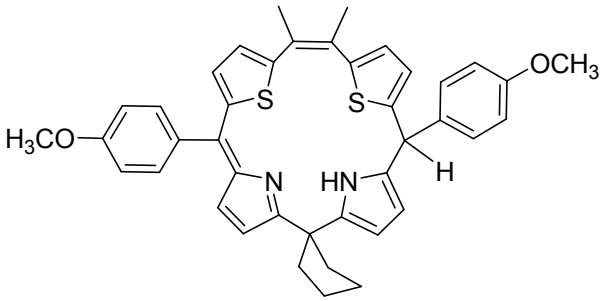


Figure S4: ^{13}C NMR spectrum of compound **3a** recorded in $CDCl_3$



3b

Indian Institute of Technology (B)

Analysis Info

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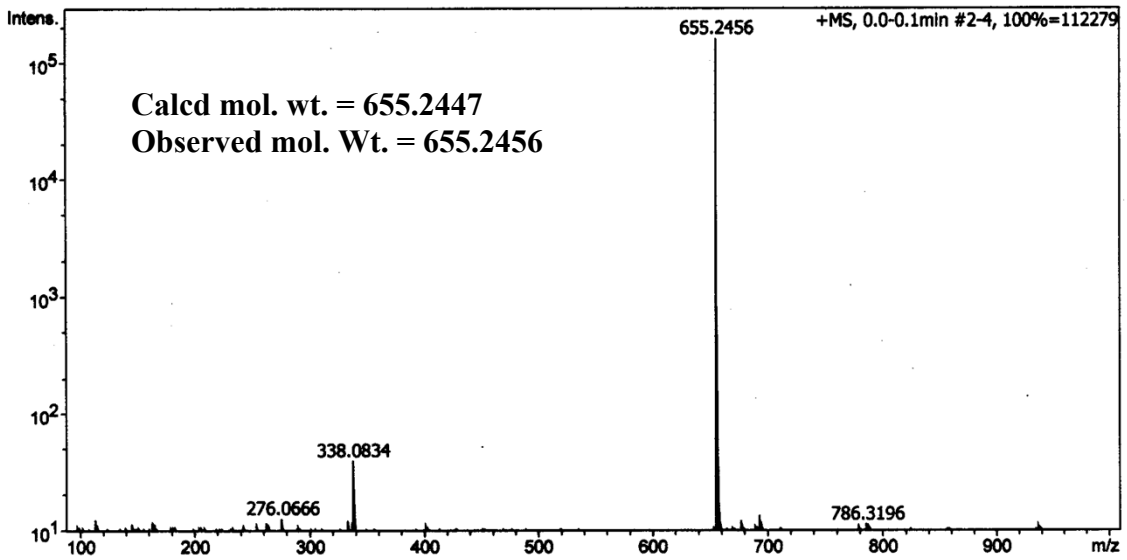
Sample Name	MR-EG-PENCALIX	Instrument	maXis impact 282001.00081
Comment	C41H38N2O2S2		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.1 Bar
Focus	Active	Set Capillary	3500 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	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
655.2456	1	C41H39N2O2S2	655.2447	-1.2	27.5	1	100.00	23.5	even	ok

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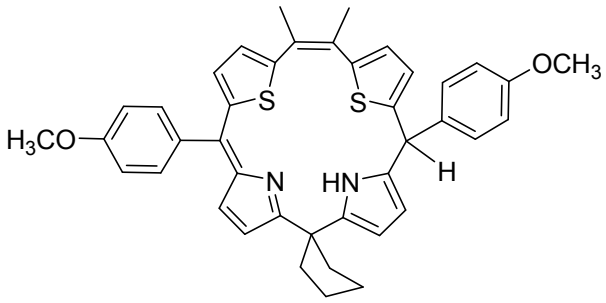
Figure S5: HRMS spectrum of compound **3b**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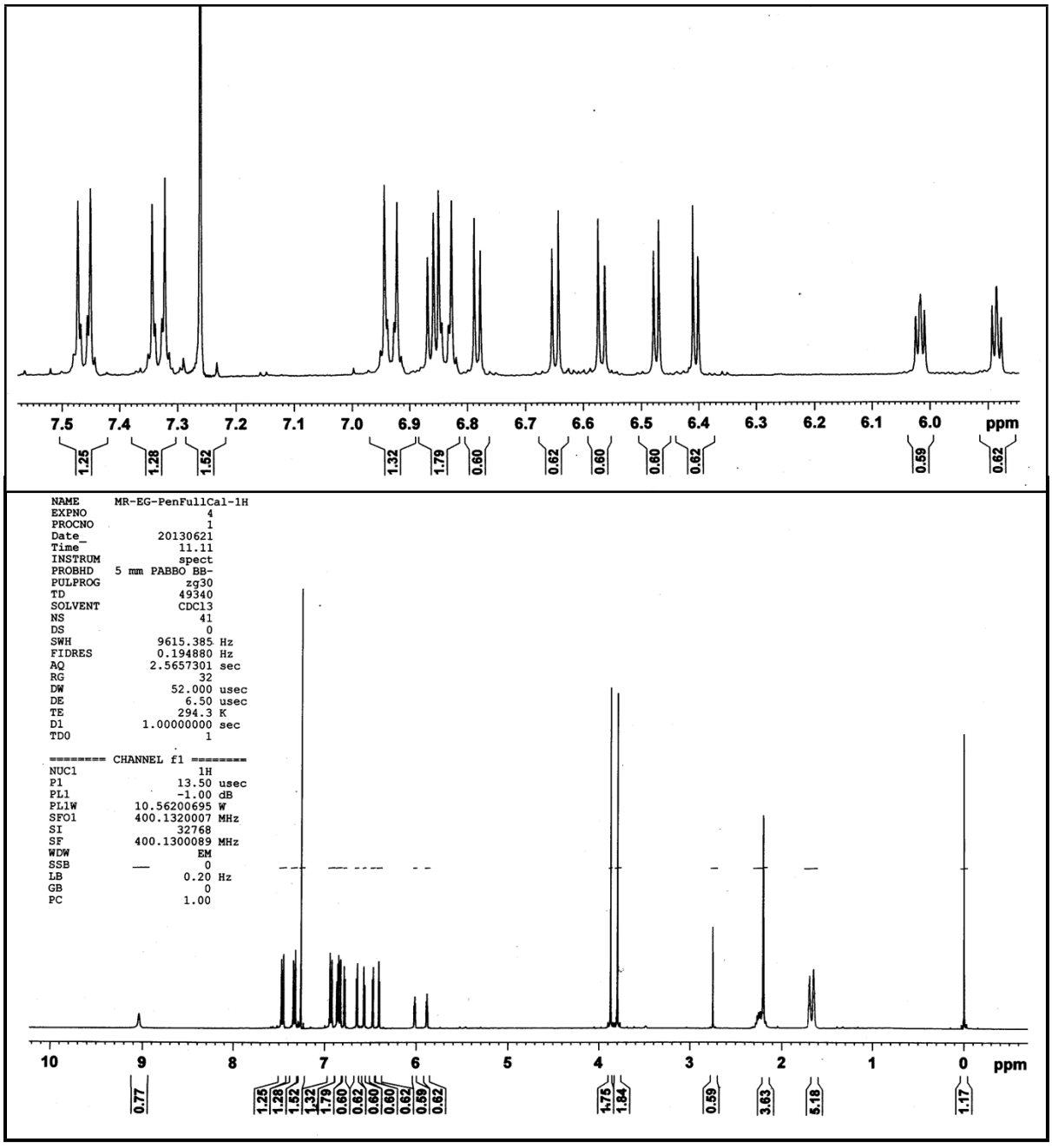
H3CO
S
S
N
HN
H

3b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1.25 1.28 1.52 1.32 1.79 0.60 0.62 0.60 0.60 0.62 0.59 0.62
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EXPNO 4
PROCNO 1
Date_ 20130621
Time 11.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 49340
SOLVENT CDCl3
NS 41
DS 0
SWH 9615.385 Hz
FIDRES 0.194880 Hz
AQ 2.5657301 sec
RG 32
DW 52.000 usec
DE 6.50 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1320007 MHz
SI 32768
SF 400.1300089 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.77 1.25 1.28 1.52 1.32 1.79 0.60 0.62 0.60 0.60 0.62 0.59 0.62 1.75 1.84 0.59 3.63 5.18 1.17

Figure S6: [1]H NMR spectrum of compound **3b** recorded in $CDCl_3$. Above shows the expansion

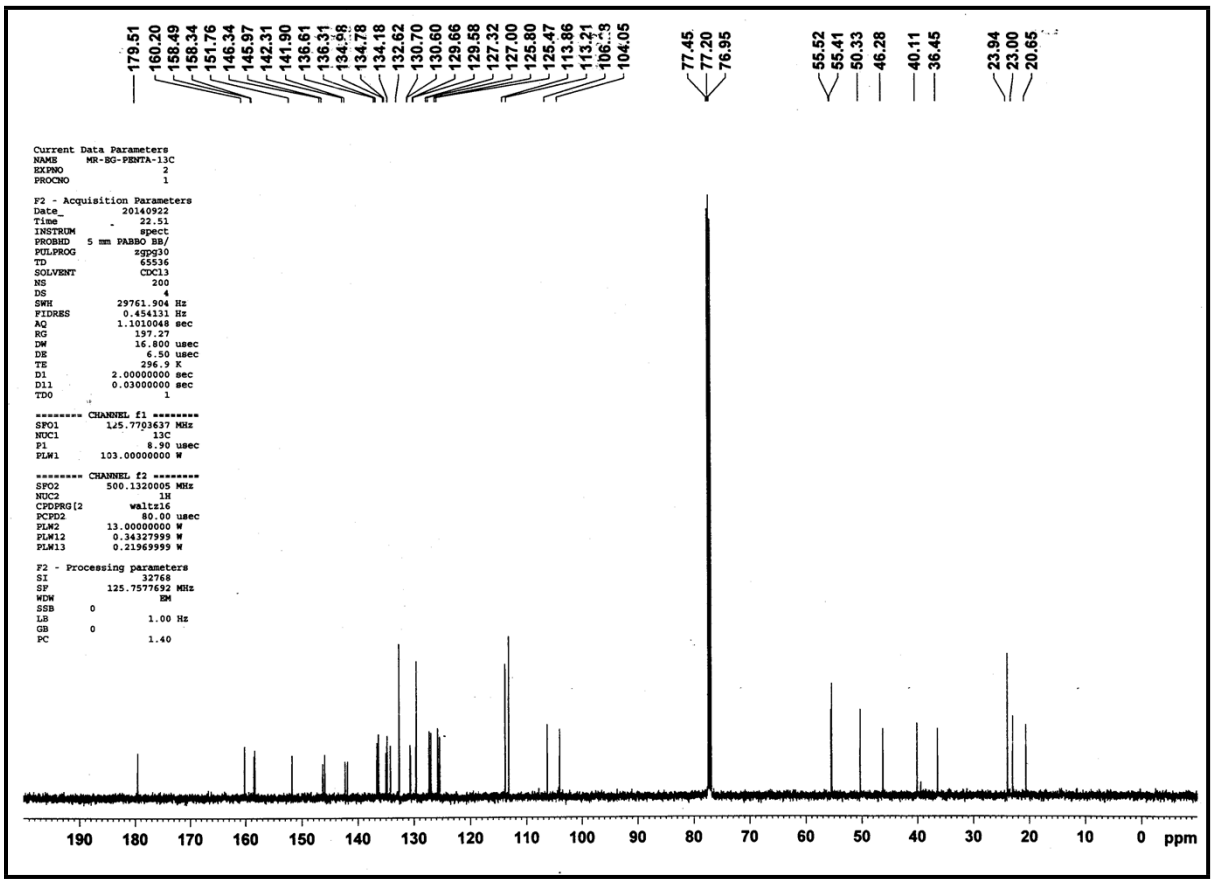
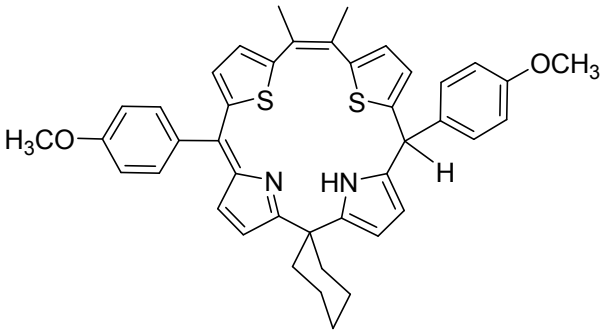


Figure S7: [13]C NMR spectrum of compound **3b** recorded in $CDCl_3$



3c

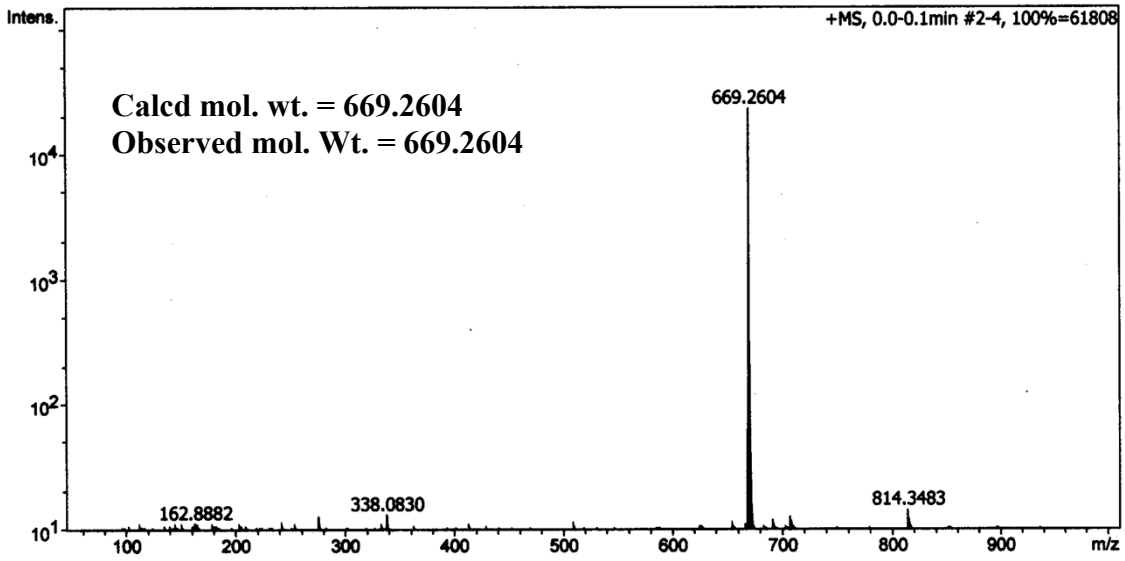
Indian Institute of Technology (B)

Analysis Info

Analysis Name	D:\Data\JUN-13\MR-EG-HEXCALIX-1.d	Acquisition Date	6/20/2013 7:20:26 PM
Method	Tune_pos_Standard_NAI-1000.m	Operator	IIT-B
Sample Name	MR-EG-HEXCALIX-1	Instrument	maXis impact 282001.00081
Comment	C42H40N2O2S2		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.1 Bar
Focus	Active	Set Capillary	3500 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	1000 m/z	Set Collision Cell RF	400.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
669.2604	1	C42H41N2O2S2	669.2604	0.0	19.8	1	100.00	23.5	even	ok

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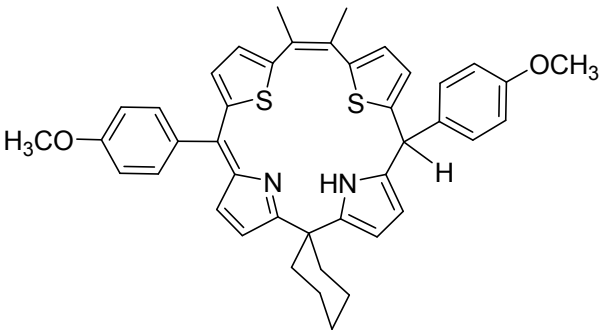
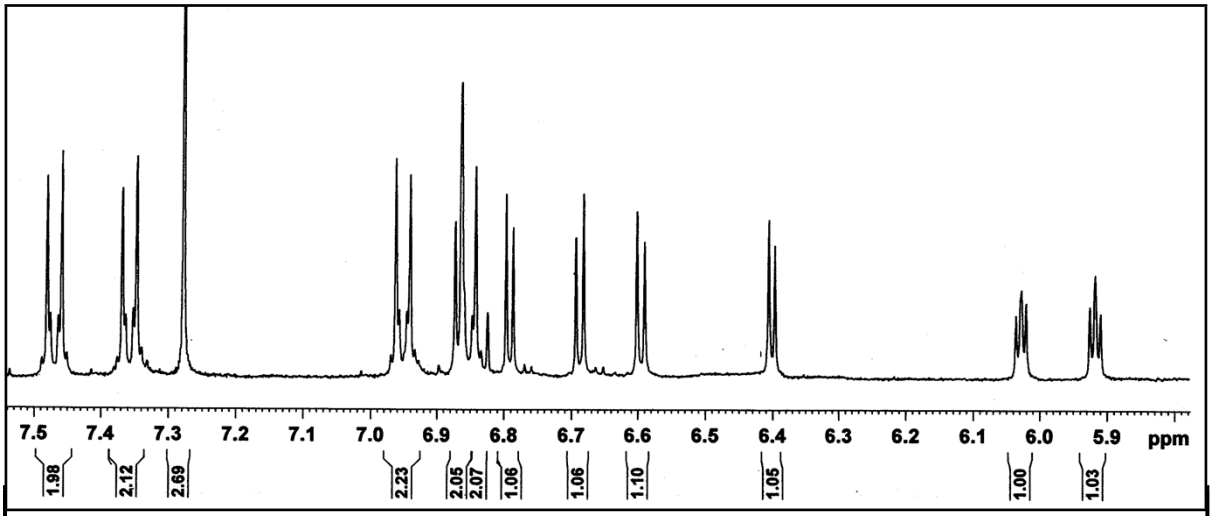
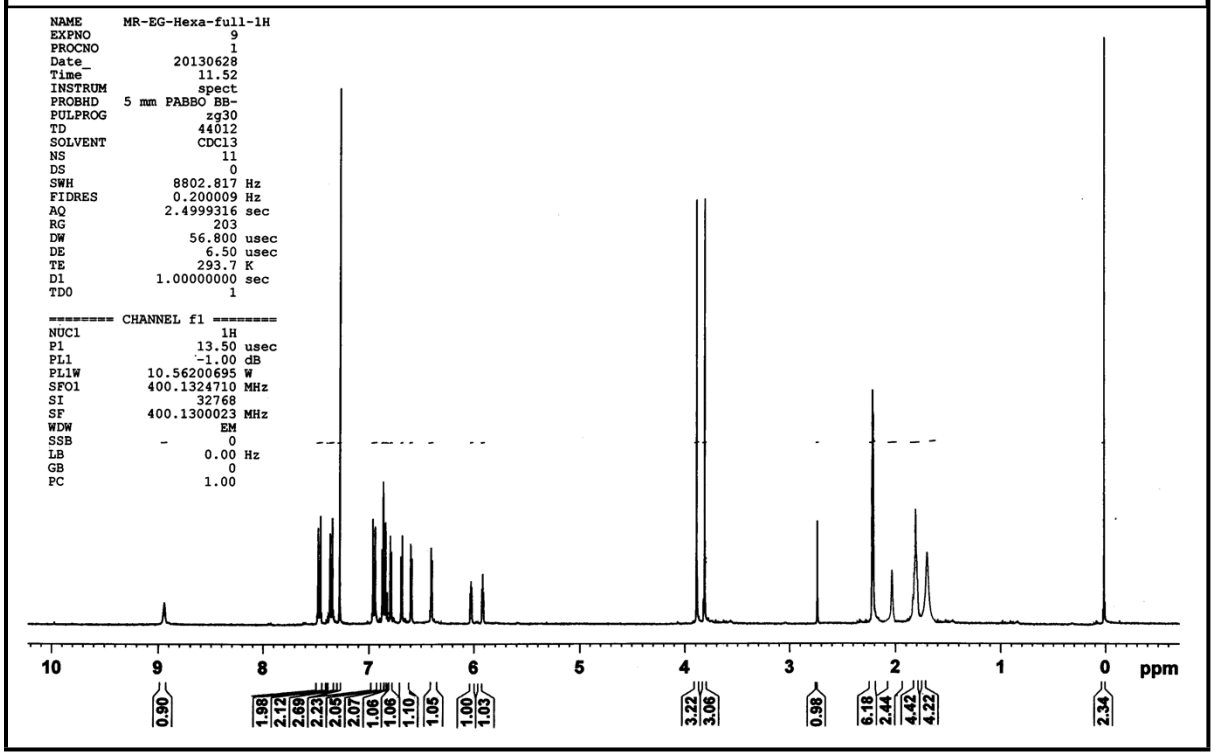
Figure S8: HRMS spectrum of compound **3c**


OCH3
S
S
H3CO
N
HN
H

3c


7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 ppm
1.98 2.12 2.69 2.23 2.05 2.07 1.06 1.06 1.10 1.05 1.00 1.03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PROCNO 1
Date_ 20130628
Time 11.52
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PULPROG zg30
TD 44012
SOLVENT CDCl3
NS 11
DS 0
SWH 8802.817 Hz
FIDRES 0.200009 Hz
AQ 2.4999316 sec
RG 203
DW 56.800 usec
DE 6.50 usec
TE 293.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300023 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
10 9 8 7 6 5 4 3 2 1 0 ppm
0.90 1.98 2.12 2.69 2.23 2.05 2.07 1.06 1.06 1.10 1.05 1.00 1.03 3.22 3.06 0.98 6.18 2.44 4.42 4.22 2.34

Figure S9: [1]H NMR spectrum of compound **3c** recorded in $CDCl_3$. Above shows the expansion

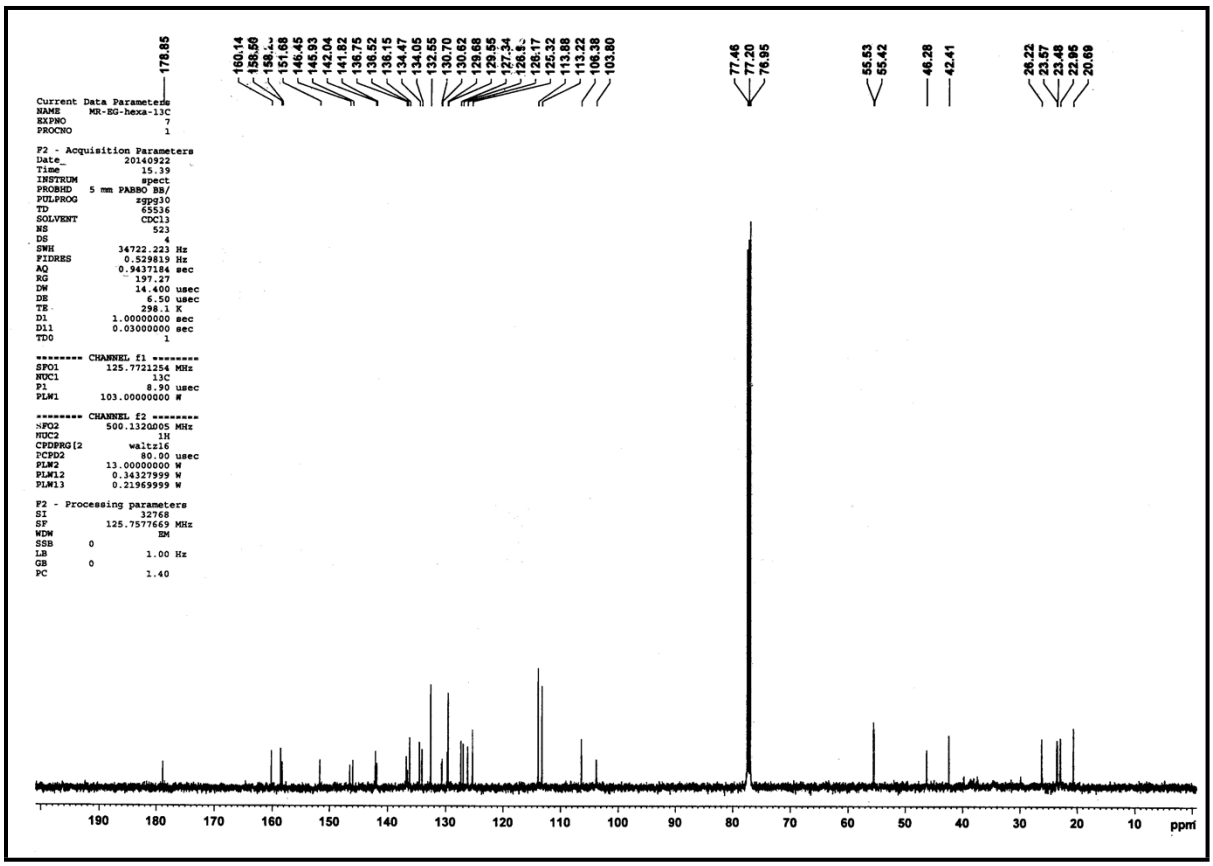

Figure S10: [13]C NMR spectrum of compound **3c** recorded in $CDCl_3$

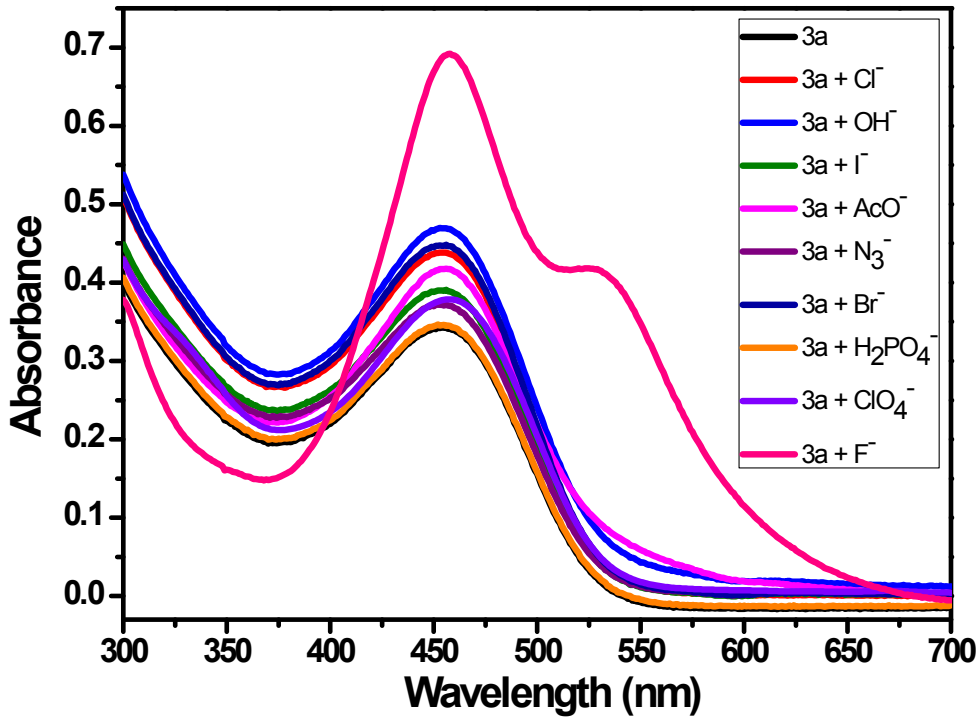

Figure S11: Absorption spectra of macrocycle **3a** (5 X 10^{-5} M) in presence of various anions (tetrabutyl ammonium salt) recorded in CH_3CN solvent.

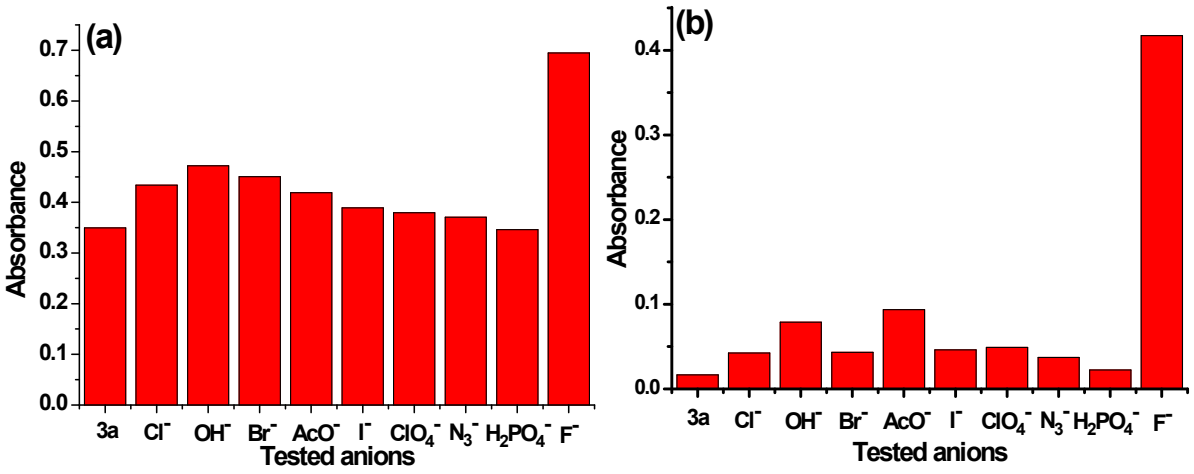

Figure S12: UV-Visible absorbance response of **3a** (5 X 10^{-5} M) at λ=454 nm (left) and 530 nm (right) in the absence and presence of the TBA salt of different anions in CH_3CN solvent.

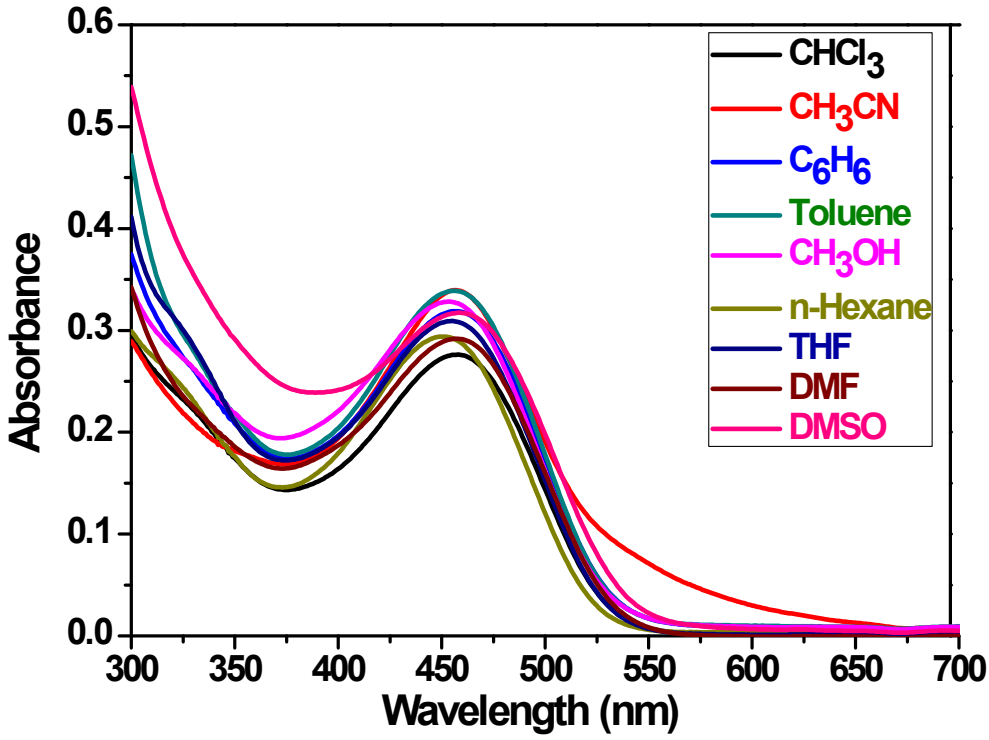

Figure S13: Absorption spectra of macrocycle **3a** (5 X 10^{-5} M) in different solvents.

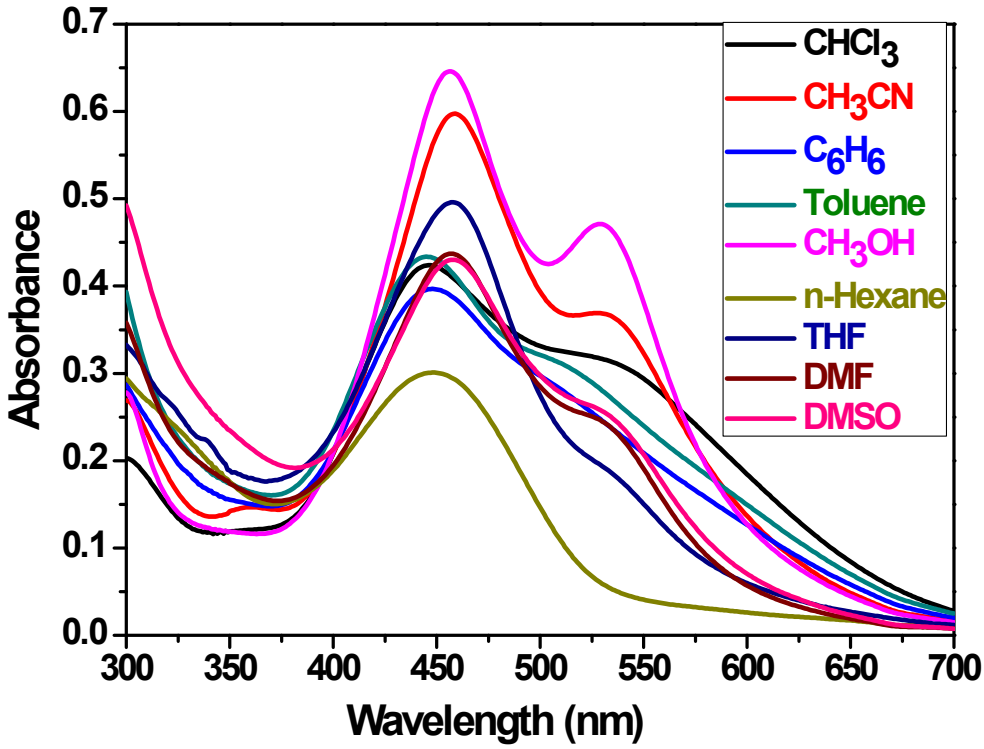

Figure S14: Absorption spectra of macrocycle **3a** (5 X 10^{-5} M) in presence of TBFA in different solvents.

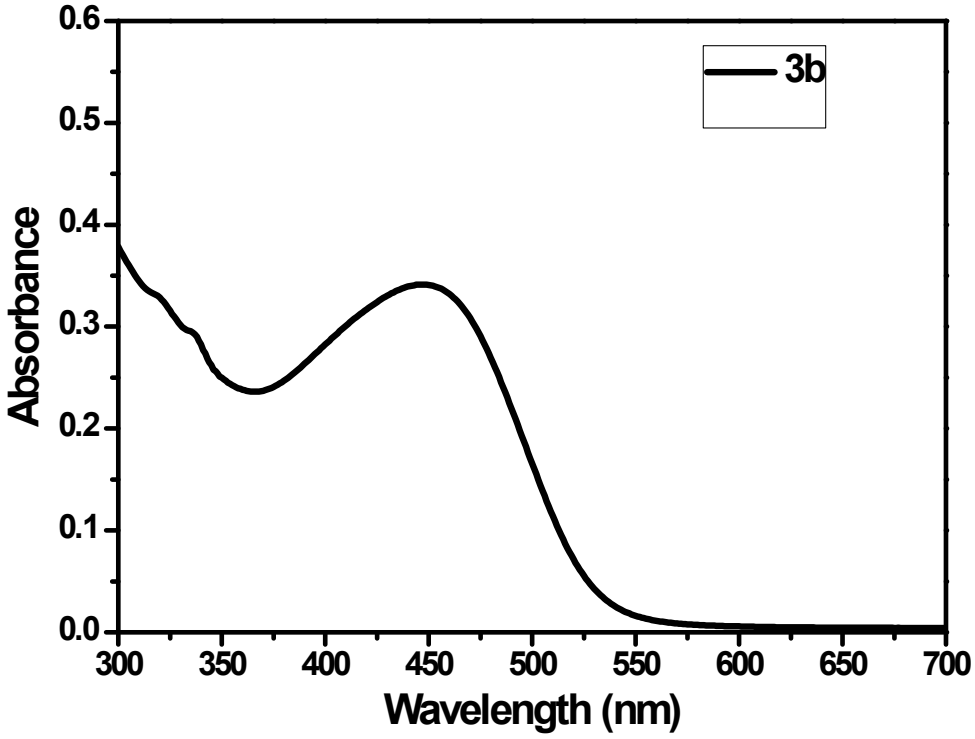

Figure S15: Absorption spectrum of macrocycle **3b** (5 X 10^{-5} M) recorded in CH_3CN solvent.

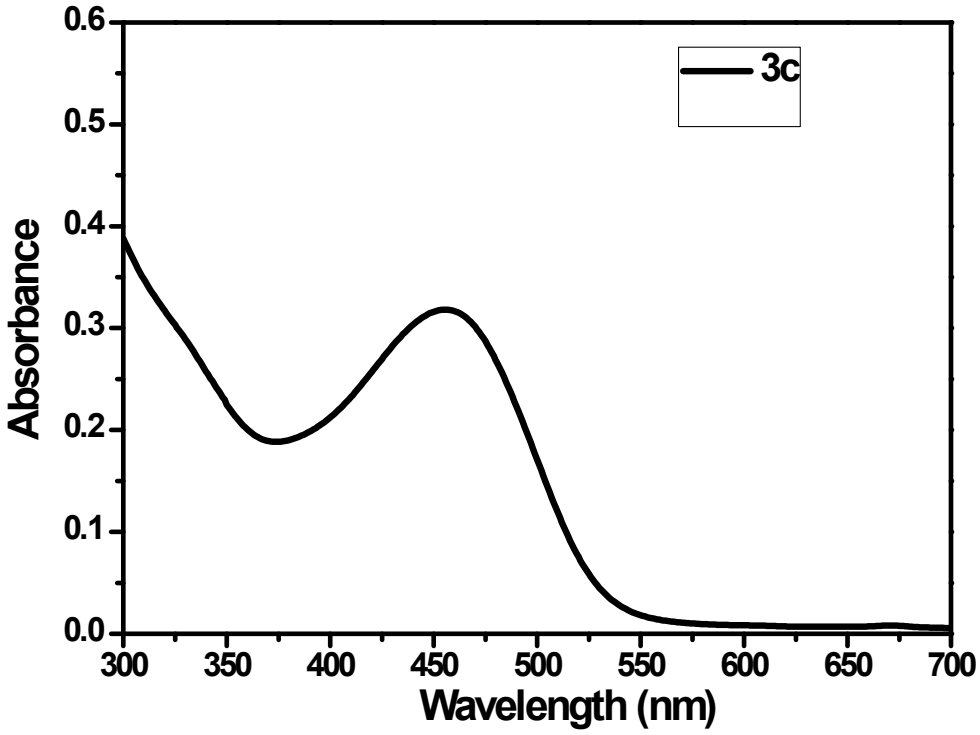

Figure S16: Absorption spectrum of macrocycle **3c** (5 X 10^{-5} M) recorded in CH_3CN solvent.

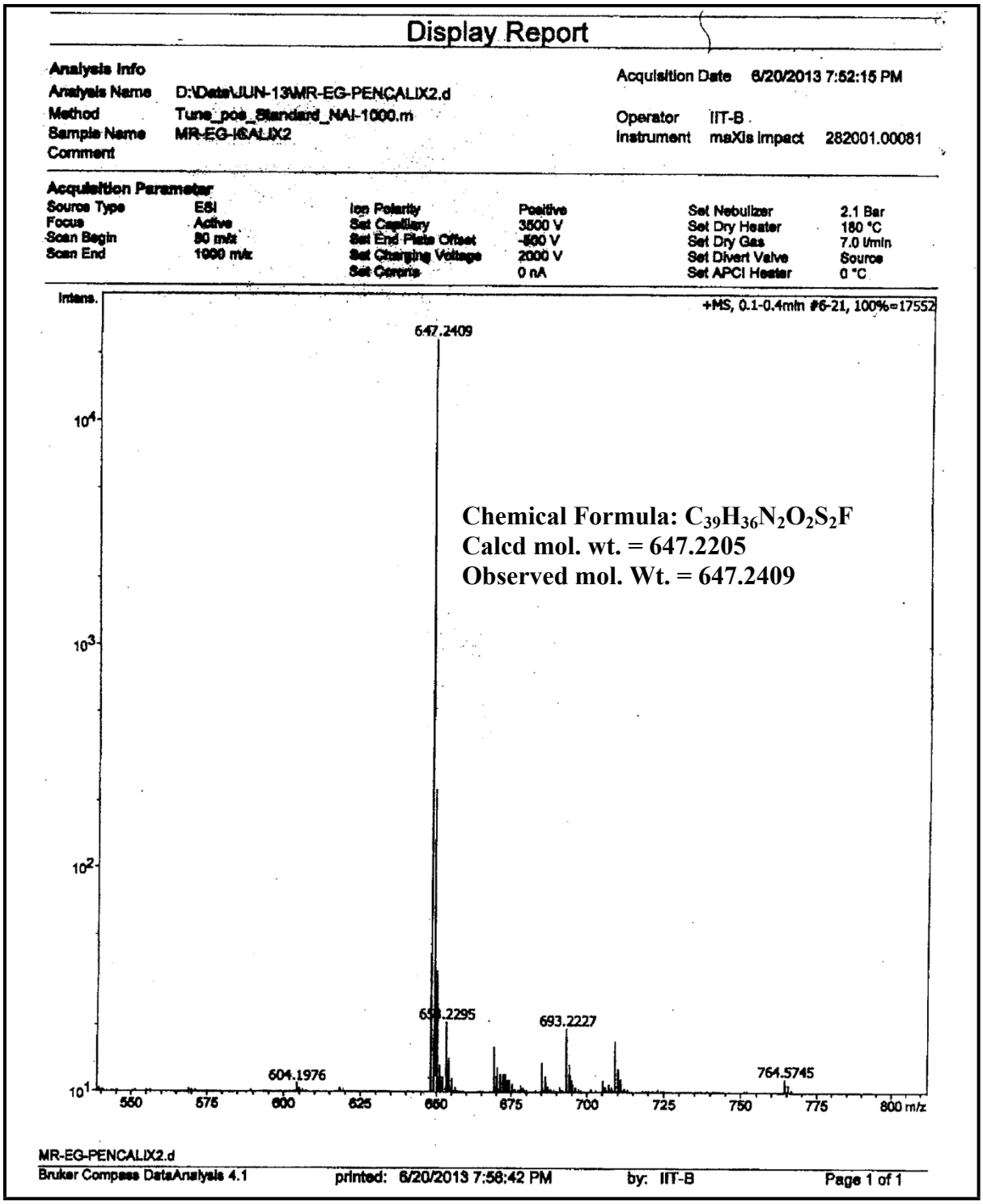

Figure S17: ES-MS spectrum of macrocycle **3a** complexed with F^- (**3a.**F^-)

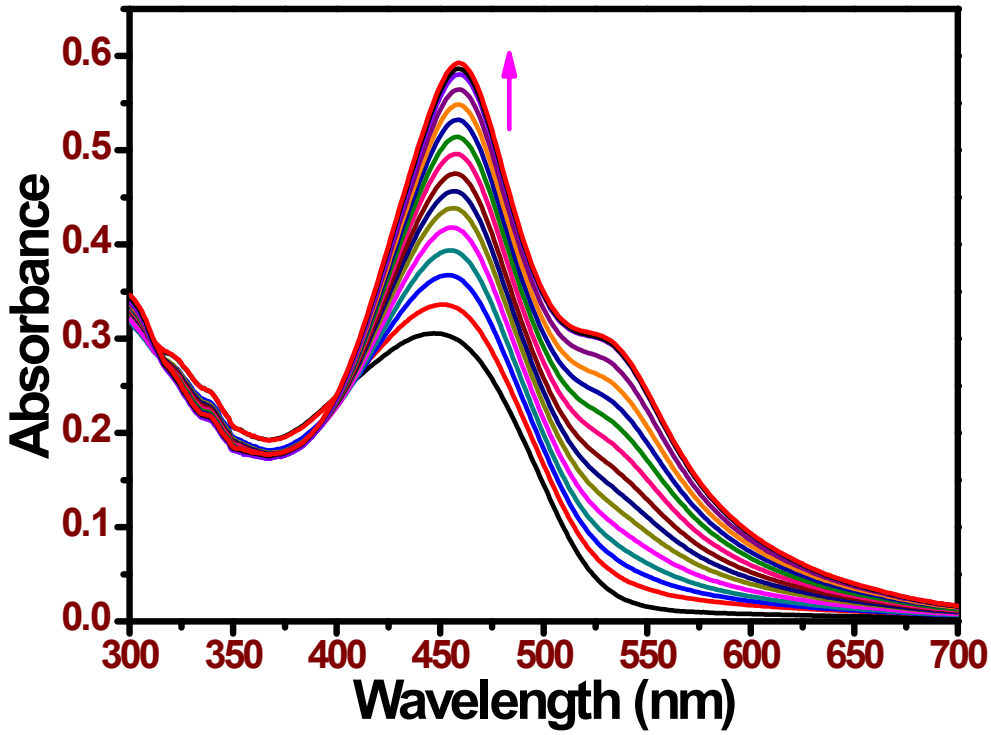

Figure S18: Absorption spectral changes of expanded dithiacalixphyrin **3a** (5 x 10^{-5} M) upon addition of increasing equivalents of F^- ions (0-7 equiv) in THF solution.