Electronic Supplementary Information

High singlet oxygen production and negative solvatochromism of octabrominated 3-pyrrolyl boron dipyrromethenes†

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Experimental Section

Chemicals. $BF_3.OEt_2$ and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) obtained from Spectrochem (India) were used as obtained. Column chromatography was performed on silica (60-120 mesh). All other chemicals used for the synthesis were reagent grade unless otherwise specified, the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetra-*n*-butylammonium perchlorate, (n-Bu_4N)ClO_4 used in electrochemical studies was from Fluka Chemicals.

Spectral Measurements. The UV-visible spectral measurements were carried out either on a Shimadzu Model 2550 double monochromator UV-visible spectrophotometer or a Jasco V-670 spectrophotometer. The steady-state fluorescence and phosphorescence spectra were measured by using a Horiba Jobin Yvon Nanolog UV-visible-NIR spectrofluorimeter equipped with a PMT (for UV-visible) and InGaAs (for NIR) detectors. A right angle detection method was used for emission measurements. For phosphorescence measurements, a pulsed xenon lamp was used. The ^1H, ^{11}B, ^{13}C and ^{19}F NMR studies were carried out on a 400 MHz and 500 MHz instruments in $CDCl_3$, tetramethylsilane (TMS) was used as an internal standard. The HRMS spectra were recorded with Bruker maxis impact 282001.00081 using electron spray ionization method and TOF analyzer. Cyclic voltammetric (CV) studies were carried out with electrochemical system utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and saturated calomel (reference electrode) electrodes. The experiments were done in dry dichloromethane using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte (TBAP). Half wave potentials were measured using DPV and also calculated manually by taking the average of the cathodic and anodic peak potentials.

X-ray crystal structure analysis:

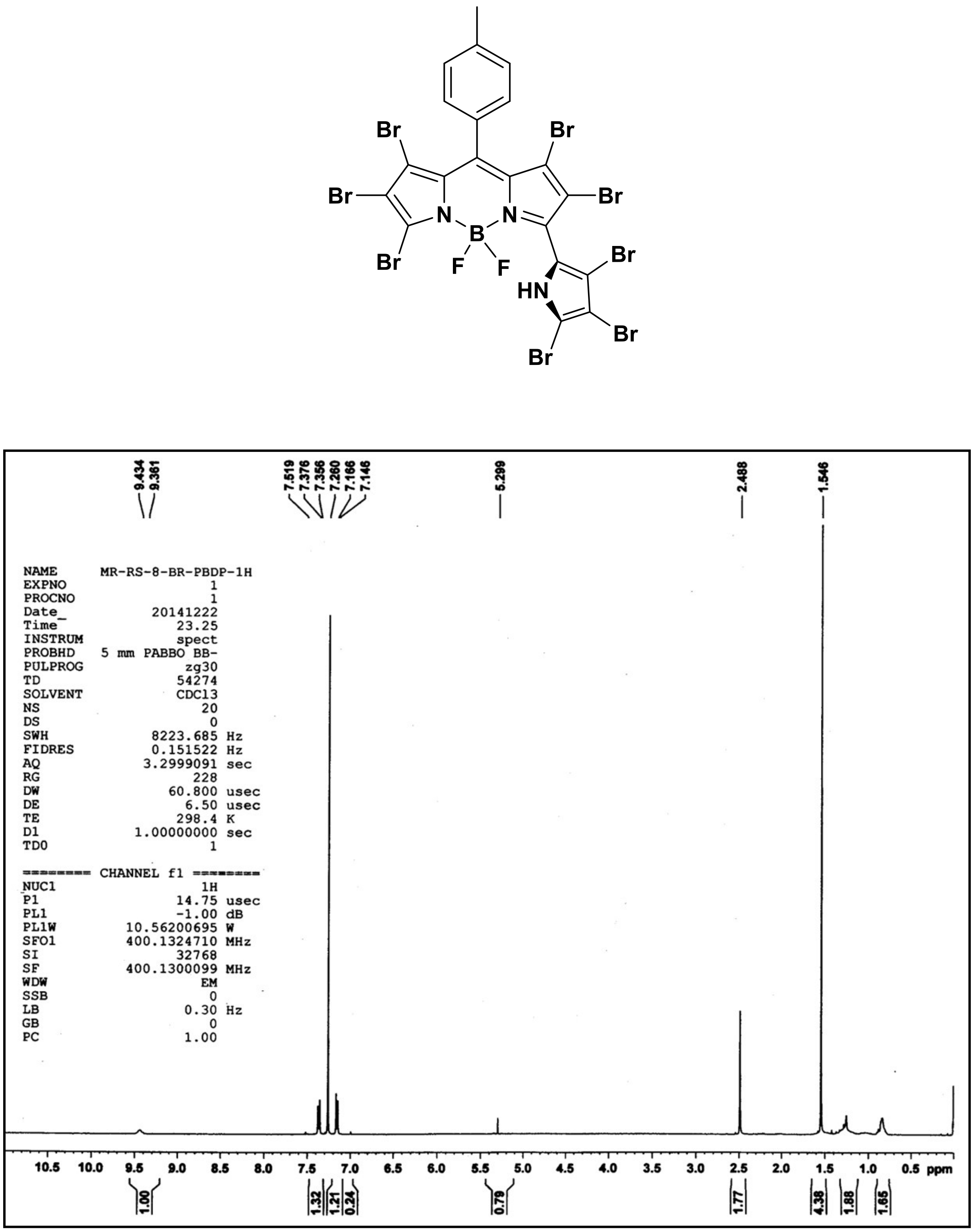
Single-crystal X-ray structure analysis was performed on a Rigaku Saturn724 diffractometer that was equipped with a low-temperature attachment. Data were collected at 100 K using graphite-monochromated Mo-K_α radiation (λ_α= 0.71073 Å) with the ω-scan technique. The data were reduced by using CrystalClear-SM Expert 2.1 b24 software. The structures were solved by direct methods and refined by least-squares against F^2 utilizing the software packages SHELXL-97,[2] SIR-92,[3] WINGX[4] and OLEX2.[5] All non-hydrogen atoms were refined anisotropically.

General experimental procedure for compounds 2a and 2b

Sample of 3-pyrrolyl BODIPY **1a**/**1b** (1 equiv.) was dissolved in 10 mL CH_2Cl_2 and nitrogen was purged for 5 minutes. Bromine (400 equiv.) was added to this solution and stirred at room temperature for 5 minutes. The progress of the reaction was monitored by TLC analysis by taking aliquots of the reaction mixture at frequent intervals. After completion of the reaction as judged by TLC analysis, the reaction mixture was diluted with CH_2Cl_2 and washed thoroughly with saturated solution of sodium thiosulphate. The organic layers were combined and dried over anhydrous sodium sulphate. The solvent was evaporated to dryness on rotary evaporator under vacuum. The crude compound was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (97:3 v/v) as eluent and desired pure product 2a/2b was obtained as dark solid.

2a: Yield, 90%; ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.48 (s, 3 H) 7.15 (d, *J*=8.04 Hz, 2 H) 7.36 (d, *J*=8.80 Hz, 2 H) 9.47 (br. s., 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 140.9, 128.6, 127.0, 120.7, 105.9, 105.8, 105.0, 21.8; ^{19}F NMR (470.5 MHz, $CDCl_3$, δ in ppm) –127 (q, ^3J(B,F), –151 (q, ^3J(B,F); ^{11}B NMR (160.MHz, $CDCl_3$, δ in ppm) 0.38 (t, ^3J(B,F);

2b: Yield, 88%; ^{1}H NMR (500 MHz, $CDCl_3$, δ in ppm): 2.48 (s, 3 H) 7.28-7.30 (m, 2 H) 7.55-7.59 (m, 3 H) 9.47 (br. s., 1 H); ^{13}C NMR (125 MHz, $CDCl_3$, δ in ppm): 144.6, 143.4, 134.9, 131.7, 130.7, 129.5, 128.9, 128.7, 125.7, 124.0, 120.6, 117.9, 106.0, 105.9, 105.0, 37.2, 32.1, 31.6, 14.3, ^{19}F NMR (470.5 MHz, $CDCl_3$, δ in ppm) –127 (q, ^3J(B,F), –151 (q, ^3J(B,F); ^{11}B NMR (160.MHz, $CDCl_3$, δ in ppm) 0.38 (t, ^3J(B,F);



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PROCNO                     1
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PULPROG                 zg30
TD                     54274
SOLVENT                CDCl3
NS                        20
DS                         0
SWH                 8223.685 Hz
FIDRES              0.151522 Hz
AQ                 3.2999091 sec
RG                       228
DW                    60.800 usec
DE                      6.50 usec
TE                     298.4 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     14.75 usec
PL1                    -1.00 dB
PL1W             10.56200695 W
SFO1             400.1324710 MHz
SI                     32768
SF               400.1300099 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
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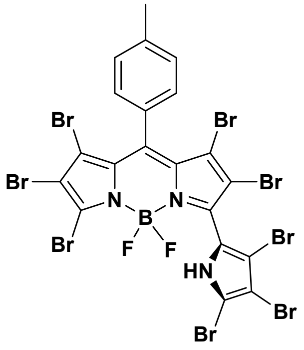
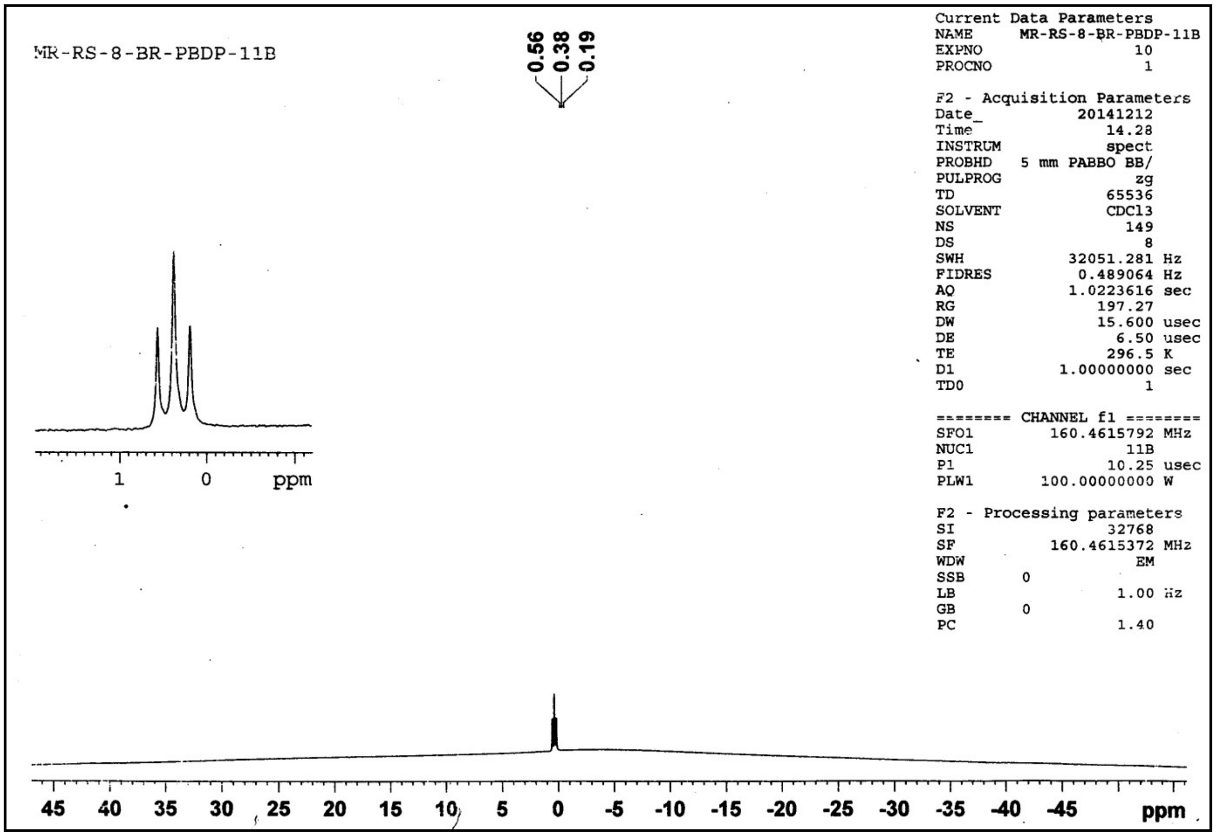
Figure S1: ^{1}H NMR spectrum of compound **2a** recorded in $CDCl_3$.





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PROCNO                     1

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Time                   14.28
INSTRUM                spect
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PULPROG                   zg
TD                     65536
SOLVENT                CDCl3
NS                       149
DS                         8
SWH                32051.281 Hz
FIDRES              0.489064 Hz
AQ                 1.0223616 sec
RG                    197.27
DW                    15.600 usec
DE                      6.50 usec
TE                     296.5 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
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NUC1                     11B
P1                     10.25 usec
PLW1            100.00000000 W

F2 - Processing parameters
SI                     32768
SF               160.4615372 MHz
WDW                       EM
SSB      0
LB                      1.00 Hz
GB       0
PC                      1.40
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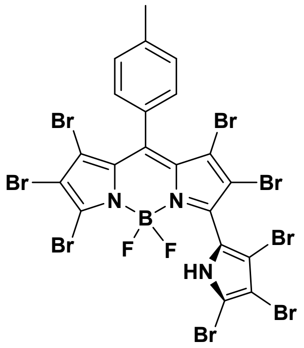
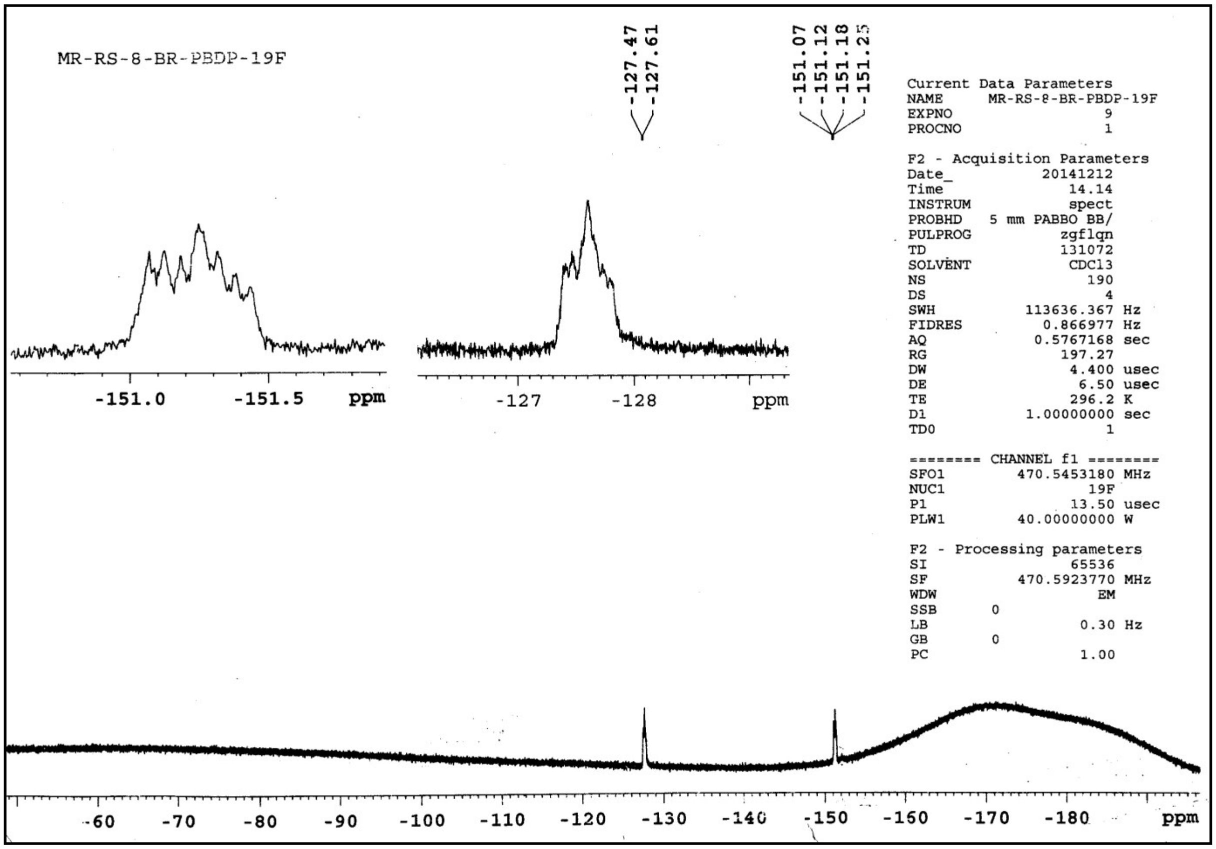
Figure S2: ^{11}B NMR spectrum of compound **2a** recorded in $CDCl_3$.





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EXPNO                    9
PROCNO                   1

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Time                 14.14
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PROBHD    5 mm PABBO BB/
PULPROG             zgflqn
TD                  131072
SOLVENT              CDCl3
NS                     190
DS                       4
SWH             113636.367 Hz
FIDRES            0.866977 Hz
AQ               0.5767168 sec
RG                  197.27
DW                   4.400 usec
DE                    6.50 usec
TE                   296.2 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           470.5453180 MHz
NUC1                   19F
P1                   13.50 usec
PLW1           40.00000000 W

F2 - Processing parameters
SI                   65536
SF             470.5923770 MHz
WDW                     EM
SSB       0
LB                    0.30 Hz
GB        0
PC                    1.00
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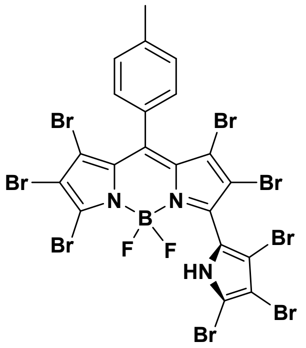
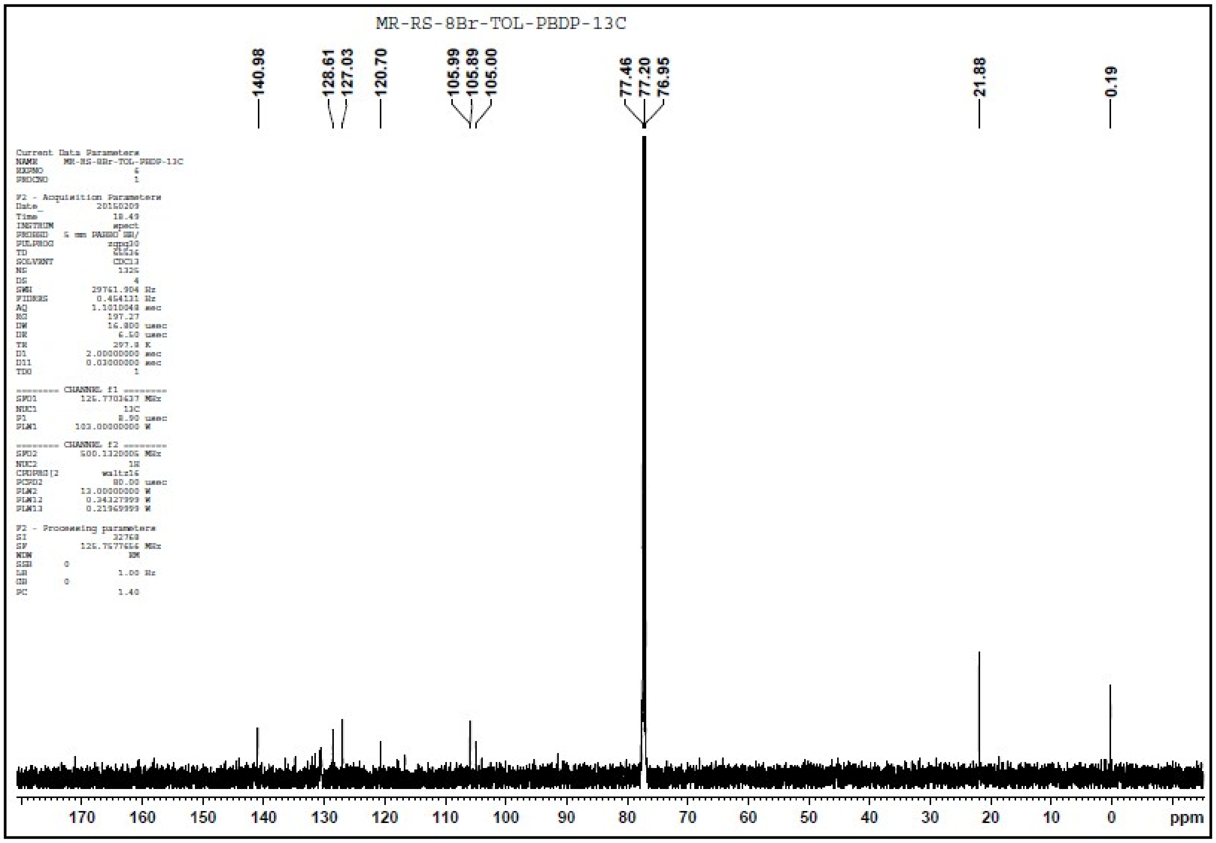
Figure S3: ^{19}F NMR spectrum of compound **2a** recorded in $CDCl_3$.





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EXPNO                     6
PROCNO                    1

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Time                  18.49
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PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     1326
DS                        4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                   197.27
DW                   16.800 usec
DE                     6.50 usec
TE                    297.8 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           125.7703637 MHz
NUC1                    13C
P1                     8.90 usec
PLW1         103.00000000 W

======== CHANNEL f2 ========
SFO2           500.1320005 MHz
NUC2                     1H
CPDPRG[2            waltz16
PCPD2                 80.00 usec
PLW2          13.00000000 W
PLW12          0.34327999 W
PLW13          0.21969999 W

F2 - Processing parameters
SI                    32768
SF             125.7577666 MHz
WDW                      EM
SSB        0
LB                     1.00 Hz
GB         0
PC                     1.40
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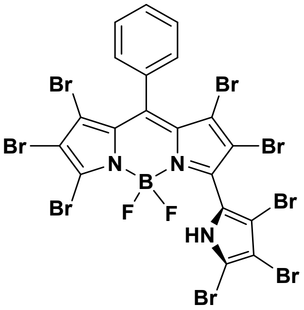
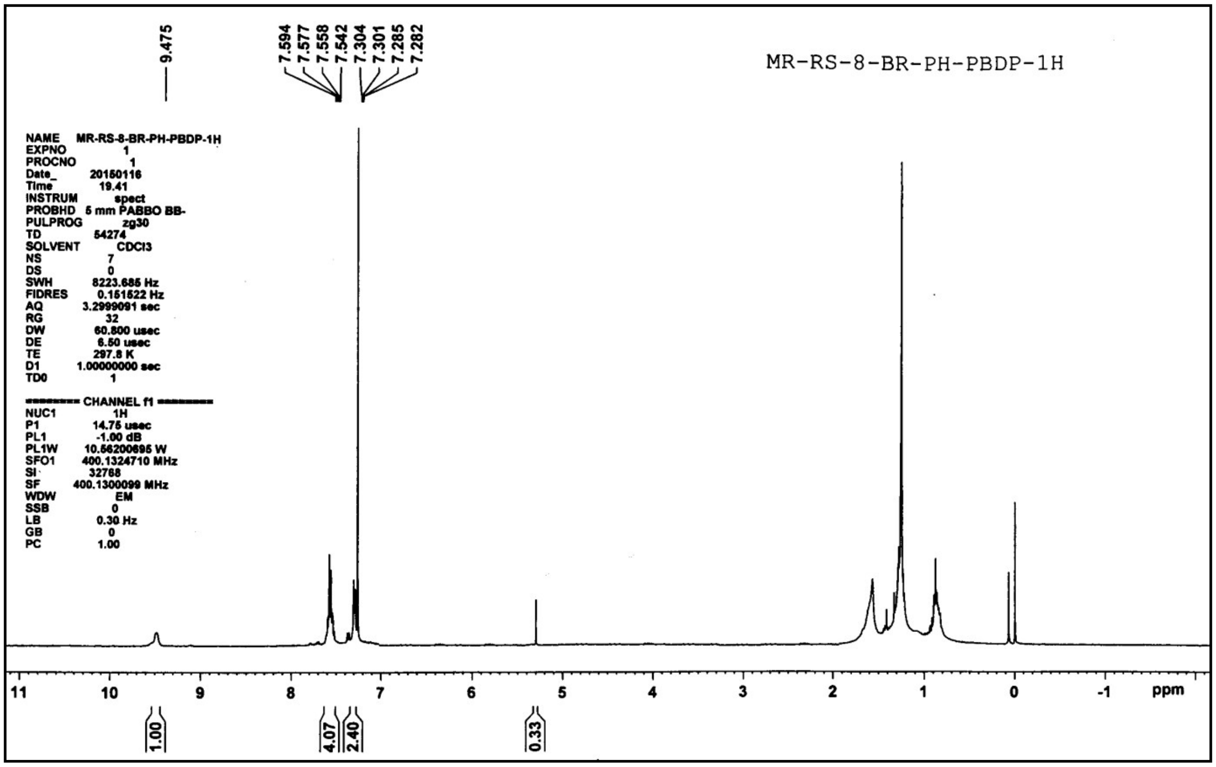
Figure S4: ^{13}C NMR spectrum of compound **2a** recorded in $CDCl_3$.





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PROCNO             1
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Time           19.41
INSTRUM          spect
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PULPROG           zg30
TD            54274
SOLVENT          CDCl3
NS                 7
DS                 0
SWH        8223.685 Hz
FIDRES     0.151522 Hz
AQ        3.2999091 sec
RG                32
DW          60.800 usec
DE            6.50 usec
TE           297.8 K
D1       1.00000000 sec
TD0                1

======== CHANNEL f1 ========
NUC1              1H
P1            14.75 usec
PL1           -1.00 dB
PL1W     10.56200695 W
SFO1     400.1324710 MHz
SI            32768
SF       400.1300099 MHz
WDW               EM
SSB                0
LB             0.30 Hz
GB                 0
PC              1.00
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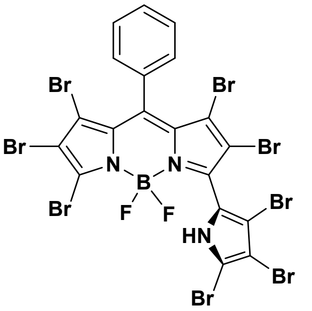
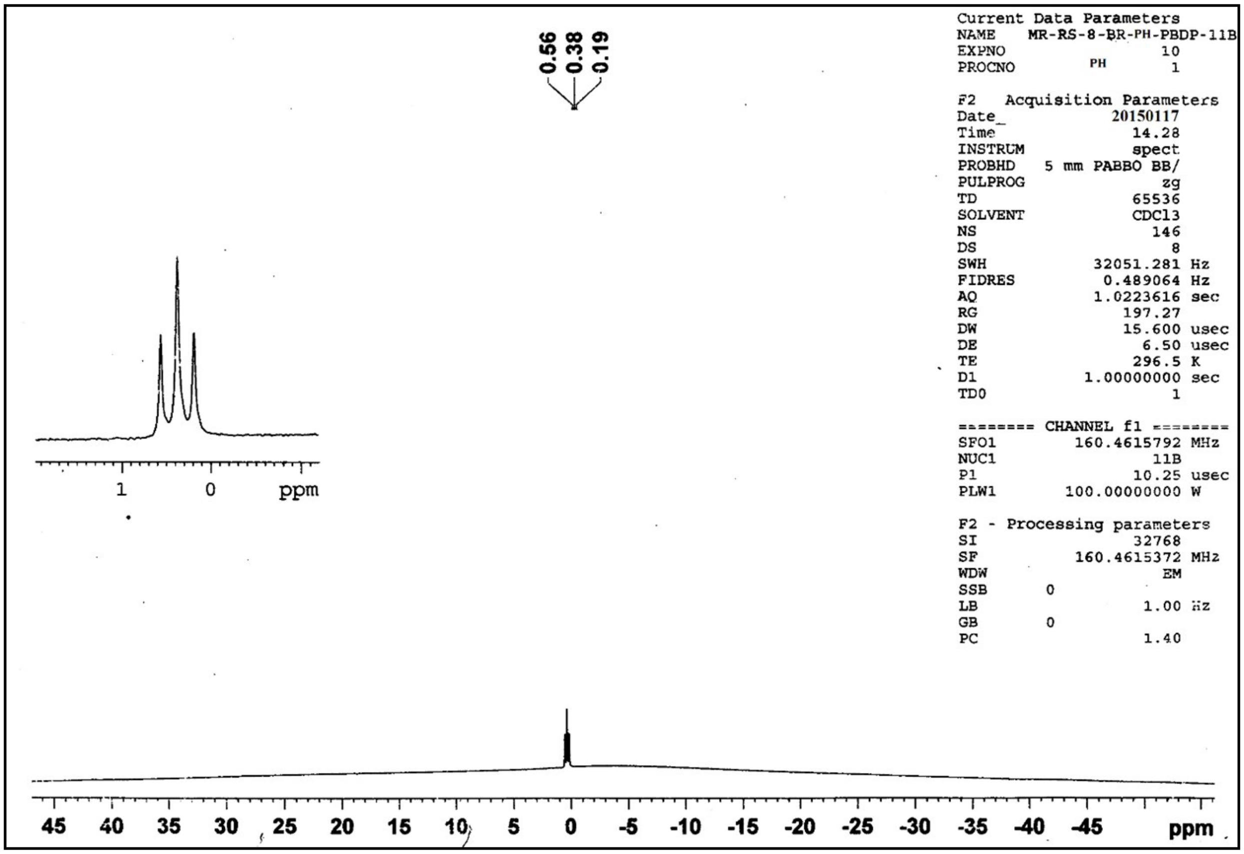
FigureS5: ^{1}H NMR spectrum of compound **2b** recorded in $CDCl_3$.





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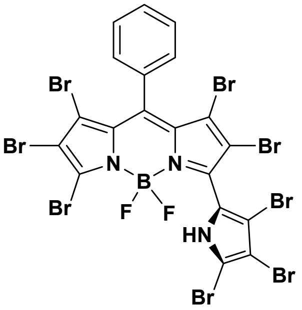
Current Data Parameters
NAME     MR-RS-8-BR-PH-PBDP-11B
EXPNO                    10
PROCNO          PH        1

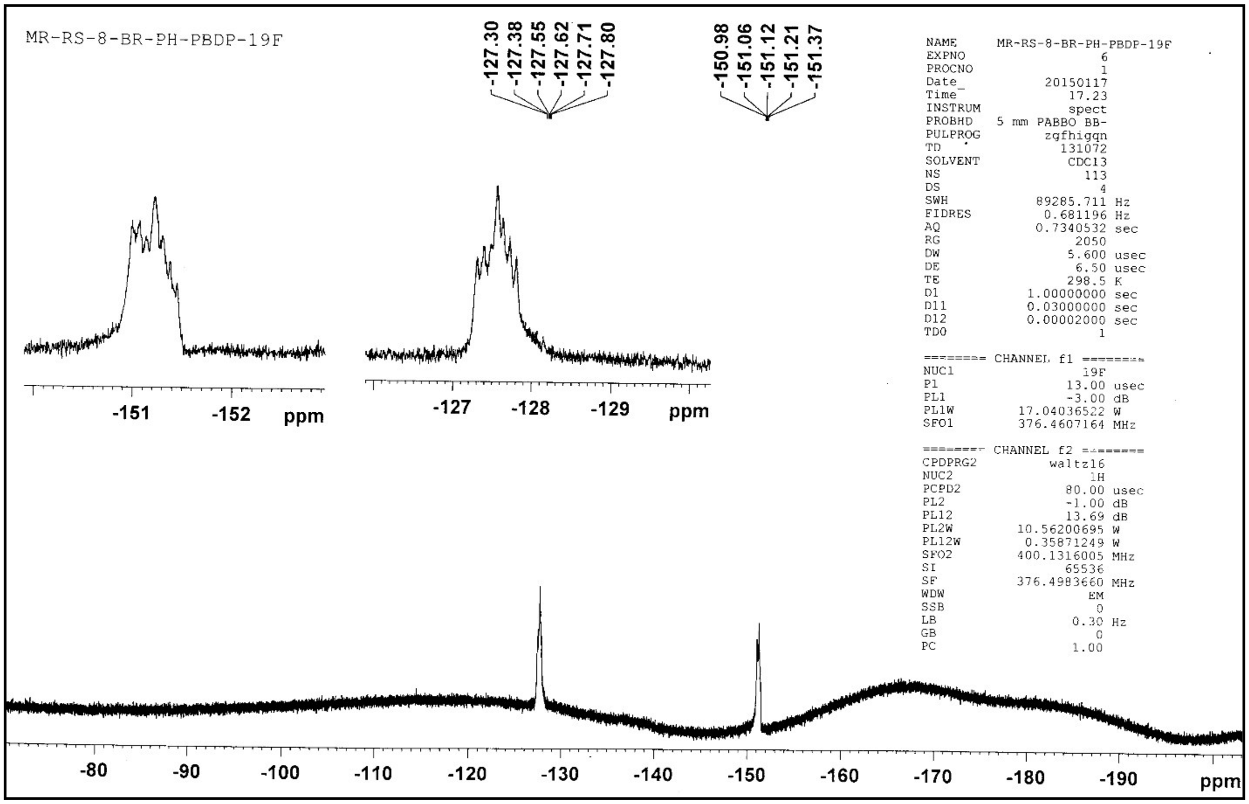
F2  Acquisition Parameters
Date_              20150117
Time                  14.28
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                  zg
TD                    65536
SOLVENT               CDCl3
NS                      146
DS                        8
SWH              32051.281 Hz
FIDRES            0.489064 Hz
AQ               1.0223616 sec
RG                   197.27
DW                   15.600 usec
DE                     6.50 usec
TE                    296.5 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1          160.4615792 MHz
NUC1                  11B
P1                   10.25 usec
PLW1          100.00000000 W

F2 - Processing parameters
SI                    32768
SF             160.4615372 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Figure S6: ^{11}B NMR spectrum of compound **2b** recorded in CDCl$_3$.





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NAME       MR-RS-8-BR-PH-PBDP-19F
EXPNO                   6
PROCNO                  1
Date_            20150117
Time                17.23
INSTRUM             spect
PROBHD     5 mm PABBO BB-
PULPROG          zgfhigqn
TD                 131072
SOLVENT             CDC13
NS                    113
DS                      4
SWH             89285.711 Hz
FIDRES           0.681196 Hz
AQ              0.7340532 sec
RG                   2050
DW                  5.600 usec
DE                   6.50 usec
TE                  298.5 K
D1             1.00000000 sec
D11            0.03000000 sec
D12            0.00002000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  19F
P1                  13.00 usec
PL1                 -3.00 dB
PL1W          17.04036522 W
SFO1          376.4607164 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -1.00 dB
PL12                13.69 dB
PL2W          10.56200695 W
PL12W          0.35871249 W
SFO2          400.1316005 MHz
SI                  65536
SF            376.4983660 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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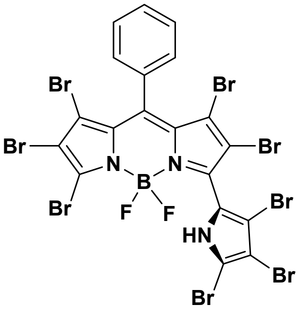
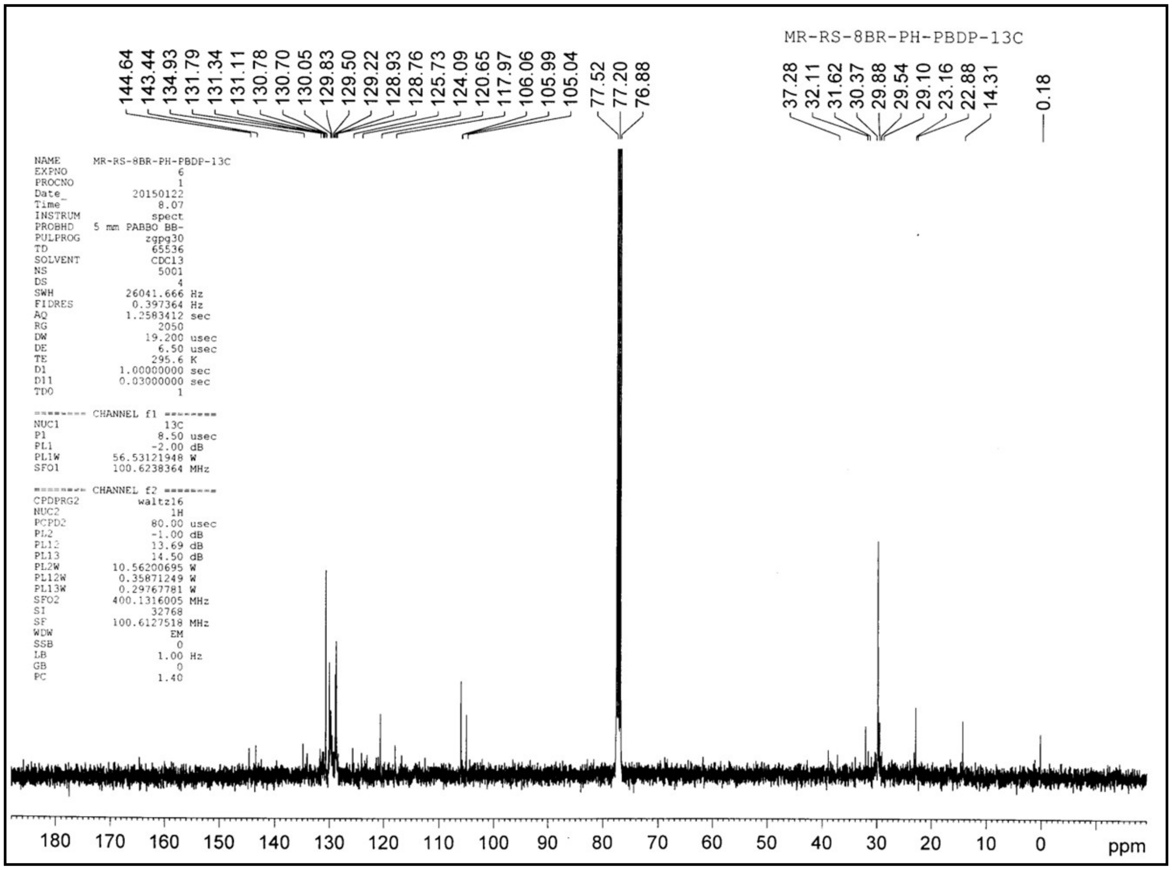
Figure S7: ^{19}F NMR spectrum of compound **2b** recorded in $CDCl_3$.





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NAME       MR-RS-8BR-PH-PBDP-13C
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PROCNO                    1
Date_              20150122
Time                   8.07
INSTRUM               spect
PROBHD     5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     5001
DS                        4
SWH               26041.666 Hz
FIDRES             0.397364 Hz
AQ                1.2583412 sec
RG                     2050
DW                   19.200 usec
DE                     6.50 usec
TE                    295.6 K
D1               1.00000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                     8.50 usec
PL1                   -2.00 dB
PL1W            56.53121948 W
SFO1            100.6238364 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 80.00 usec
PL2                   -1.00 dB
PL12                  13.69 dB
PL13                  14.50 dB
PL2W            10.56200695 W
PL12W            0.35871249 W
PL13W            0.29767781 W
SFO2            400.1316005 MHz
SI                    32768
SF              100.6127518 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
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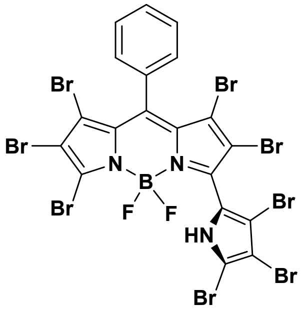
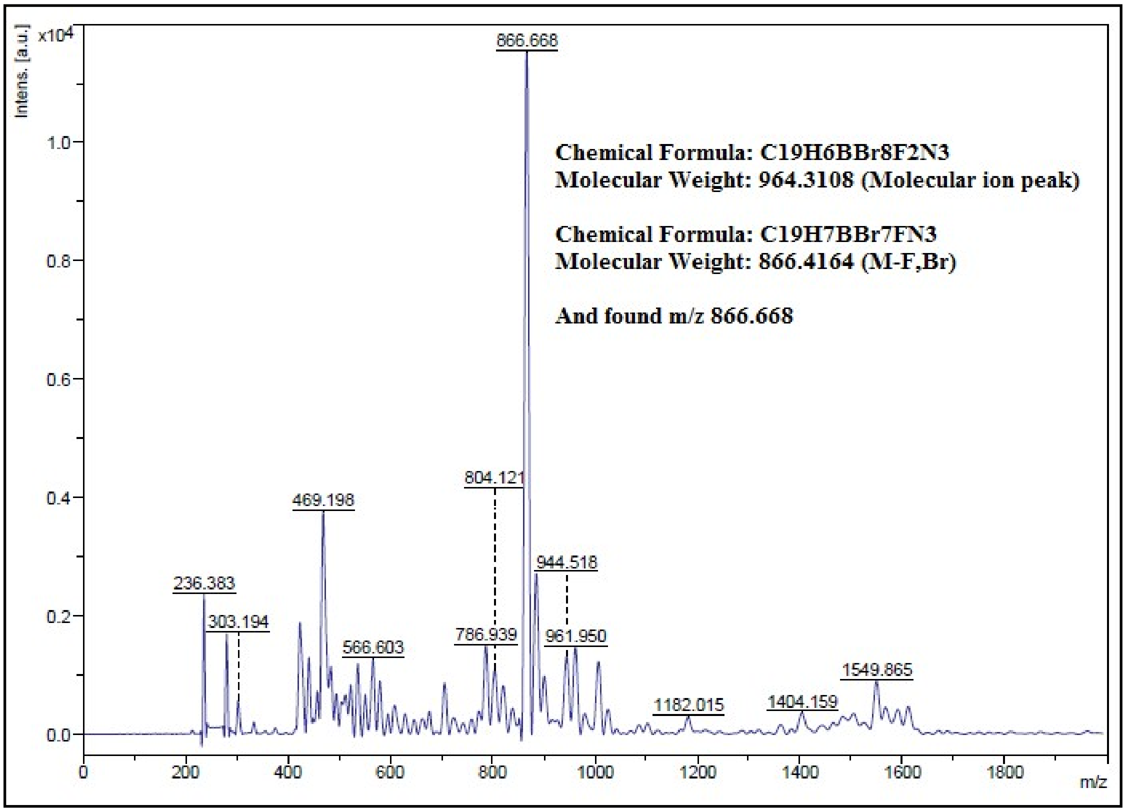
Figure S8: ^{13}C NMR spectrum of compound **2b** recorded in $CDCl_3$.





Chemical Formula: $C_{19}H_6BBr_8F_2N_3$
Molecular Weight: 964.3108 (Molecular ion peak)

Chemical Formula: $C_{19}H_7BBr_7FN_3$
Molecular Weight: 866.4164 (M-F,Br)

And found m/z 866.668

Figure S9: MALDI-TOF-Mass spectrum of compound **2b**.

Table S1: Comparison of **1c** and **2a** of crystallographic data, some selected bond lengths [Å], bond angles [°] and dihedral angles [°] obtained from X-ray crystal structure.

Parameters	**1c**[*]	**2a**
mol formula	$C_{23}H_{22}BF_2N_3O_2$	$C_{20}H_8BBr_8F_2N_3$
cryst sym	Tetragonal	Monoclinic
space group	$P\ 42/_n$	$P21/_c$
a (Å)	14.5918(2)	11.146(3)
b (Å)	14.5918(2)	9.145(2)
c (Å)	21.0203(6)	24.621(6)
α (deg)	90.00	90.00
β (deg)	90.00	101.099(4)
γ (deg)	90.00	90.00
V (Å3)	4475.66(15)	2462.7(10)
Z	8	4
B-F2	1.394	1.393
B-F1	1.394	1.370
B1-N2	1.551	1.562
B1-N1	1.526	1.552
C5-C14	1.479	1.499
F1-B-F2	108.99	110.54
C15C14C5C6	72.08	93.57

[*] data taken from reference no. 16.

Table S2: Absorption data of compounds **1a** and **2a** in different solvents.

Solvent	λ_{abs}(nm) (**2a**)	log ε_{max} (**2a**)	λ_{abs}(nm) (**1a**)	log ε_{max} (**1a**)
Toluene	613	4.79	581	4.96
Benzene	612	4.66	581	4.95
Chloroform	610	4.72	578	4.96
DCM	598	4.75	575	4.95
EtoAc	571	4.57	574	4.94
THF	555	4.57	577	4.95
CH3CN	547	4.66	570	4.91
DMF	511	4.57	579	4.93