Supporting information for:

Design and Synthesis of Perfluoroalkyl Decorated BODIPY Dye for Random Laser Action in a Microfluidic Device

Apurba Maity,[a] Anirban Sarkar,[b] Shivakiran Bhaktha B. N.[*b] and Sanjib K. Patra[*a]

[a]*Department of Chemistry, Indian Institute of Technology Kharagpur, Kharagpur 721302, INDIA*

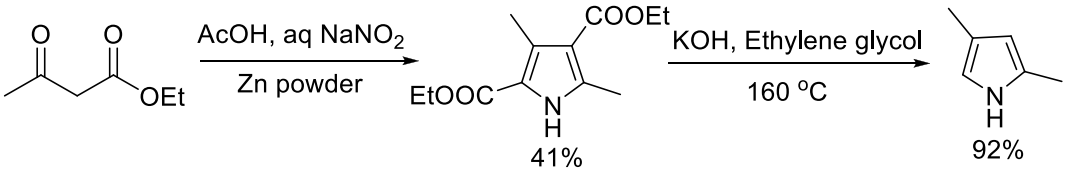
[b]*Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur 721302, INDIA*

1. Synthetic and Characterization

1.a) Materials and Methods

All moisture sensitive reactions and manipulations were carried out under an atmosphere of pre-purified Ar by using standard Schlenk techniques. The glasswares were oven-dried (at 180 ˚C) and cooled under vacuum. Tetrahydrofuran was dried over Na/benzophenone whereas dry CH_2Cl_2 and MeOH were obtained by distillation over CaH_2. Et_3N and $^iPr_2NH$ were distilled over KOH. $BF_3{\cdot}OEt_2$, NaOH and $AlCl_3$ were purchased from Spectrochem. Compound **1**[1] and 2,4-Dimethylpyrrole[2] were synthesized following previously reported literature procedure. Unless otherwise mentioned all chemicals were of analytical grade, obtained from Aldrich, and used without further purification. Phenyl acetylene, ethyl acetoacetic ester and acetyl chloride were purchased from Spectrochem and distilled prior to use. $Pd(PPh_3)_2Cl_2$ was synthesized following the procedures described in the literature.[3] Silica gel (60–120 mesh) used for column chromatography, was purchased from Merck. Eluting systems for column chromatography purifications were determined by thin layer chromatography (TLC) analysis. TLC plates were visualized under UV light (254 nm). Solvents were evaporated under reduced pressure using a rotary evaporator.

1.b) Synthesis



2,4-Dimethyl-1H-pyrrole: It was synthesized from diethyl 3,5-dimethyl-1H-pyrrole-2,4-dicarboxylate[4] according to the literature procedure.[5] ^{1}H NMR (400 MHz $CDCl_3$): δ 7.62 (br s, 1H, pyrrole N-H), 6.41(s, 1H, pyrrole H), 5.75(s, 1H, pyrrole H), 2.24 (s, 3H, pyrrole-CH_3), 2.08 (s, 3H, pyrrole-CH_3).

Synthesis of 1:[1] In an oven dried 250mL Schlenk flask, acetyl chloride (0.22 mL, 0.25 g, 3.15 mmol) was added dropwise to a solution of 2,4-dimethylpyrrole (0.65 mL, 0.6 g, 6.3 mmol) in anhydrous CH_2Cl_2 (100 mL) via syringe under argon atmosphere and the mixture was stirred at room temperature overnight. Then Et_3N (6 mL, 43 mmol) followed by $BF_3{\cdot}Et_2O$ (6 mL, 45-50%

BF_3 in ether) were added under ice-cold condition, and the reaction mixture was stirred for additional 1 h. After that, the reaction mixture was poured into distilled water (100 mL). Organic layer was extracted with dichloromethane (DCM), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was further purified using column chromatography (silica gel 60-120, CH_2Cl_2: hexane = 1:1) to give compound **1** as red powder. Yield: 0.35 g (42%). ^{1}H NMR (400 MHz, $CDCl_3$): 6.05 (s, 2H, pyrrole-H), 2.58 (s, 3H, meso-CH_3), 2.52 (s, 6H, pyrrole-CH_3), 2.41 (s, 6H, pyrrole-CH_3). ^{13}C{H} NMR ($CDCl_3$, 100 MHz): δ 153.8, 141.6, 141.2, 132.3, 121.5 (BODIPY core), 17.5, 16.9, 14.6 (-CH_3). ^{19}F{H} NMR (376 MHz, $CDCl_3$): δ -146.7 (q, J_{BF} = 34.0 Hz). HRMS (ESI$^+$, m/z): $[M+H]^+$ calcd for $C_{14}H_{18}BF_2N_2$ 263.1531, found 263.1547.

1.c) NMR Spectra

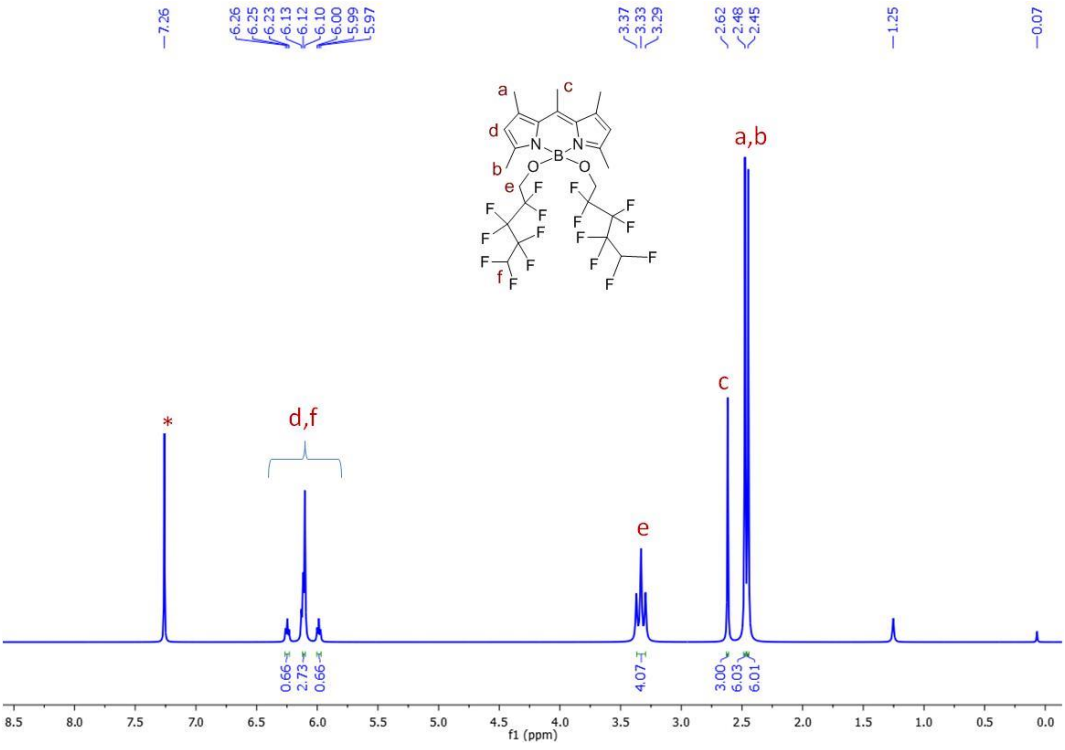


Fig S1a: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.

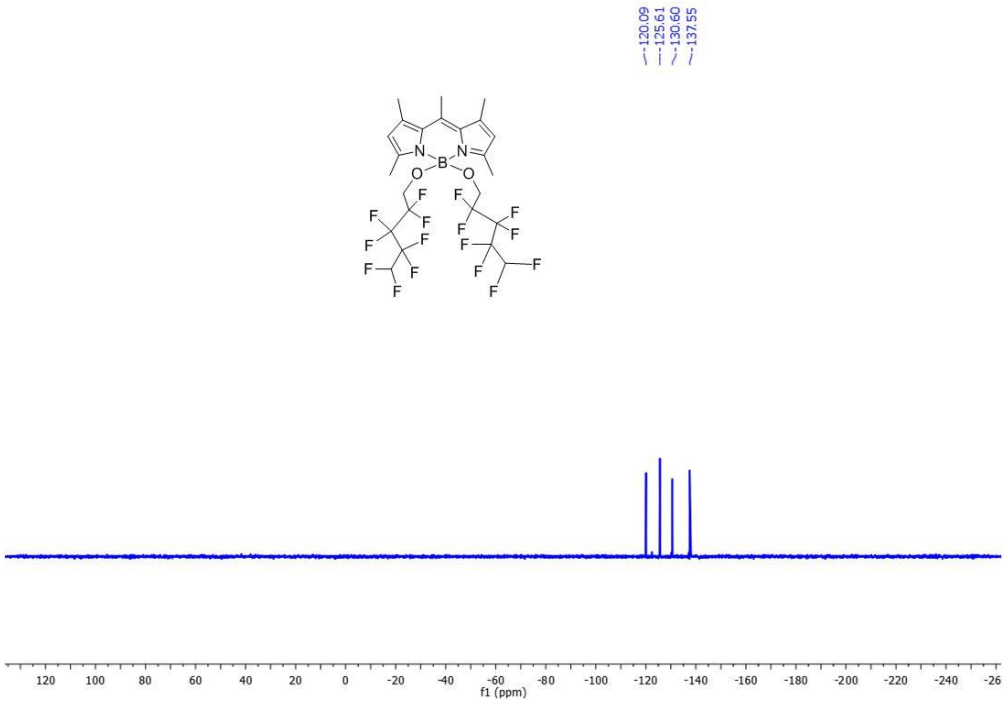


Fig S1b: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **2**.

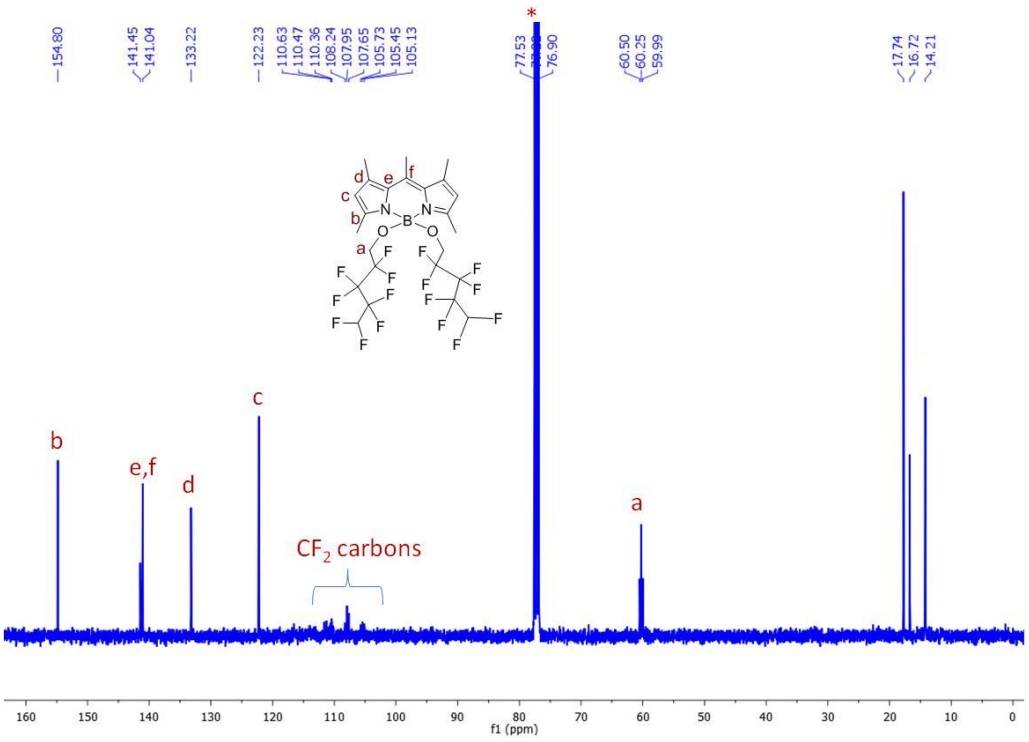


Fig S1c: $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) spectrum of **2**.

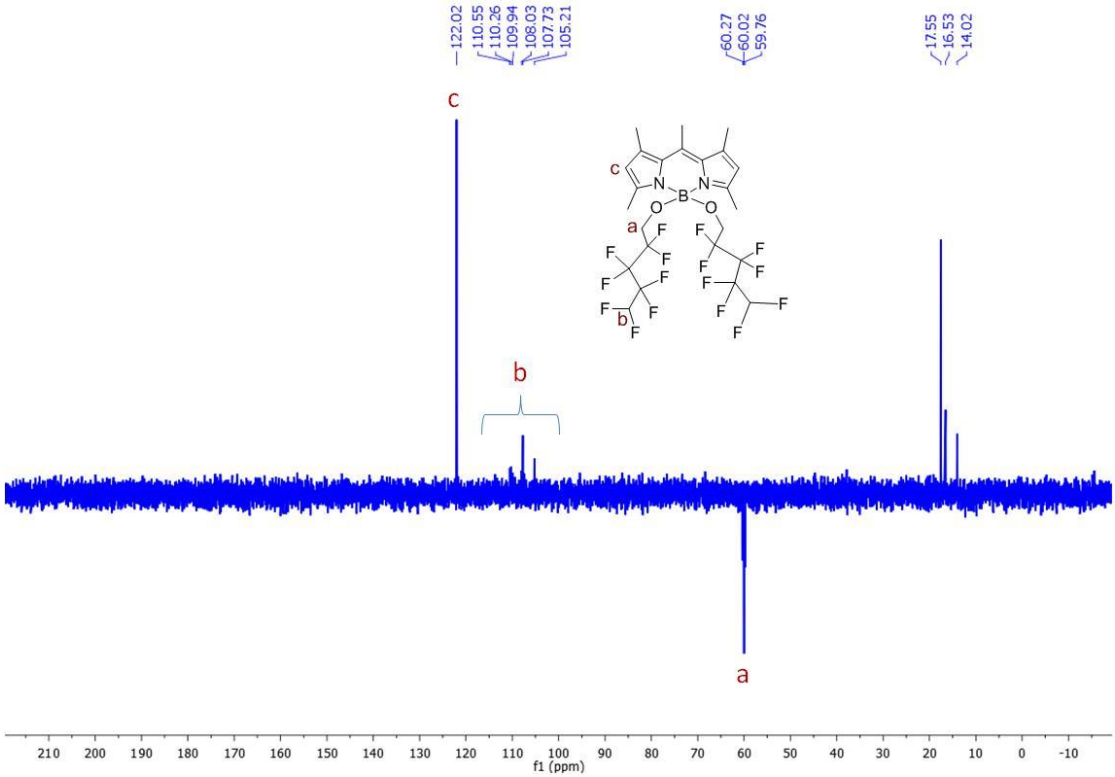


Fig S1d: DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of **2**.

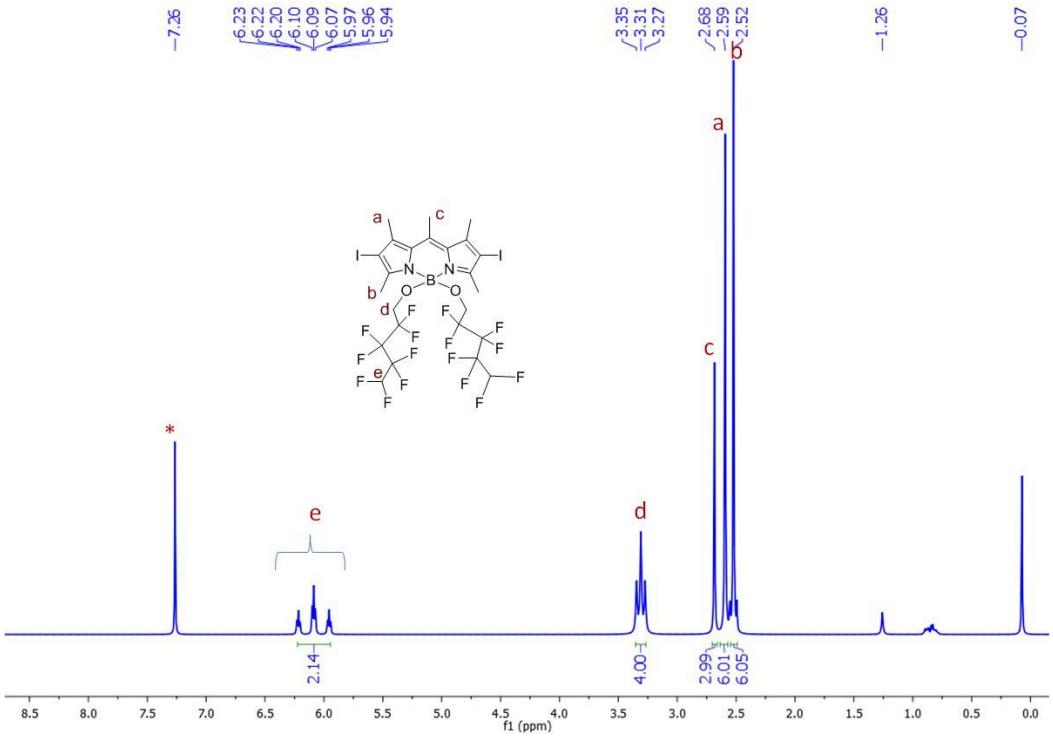


Fig S2a: ^1H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

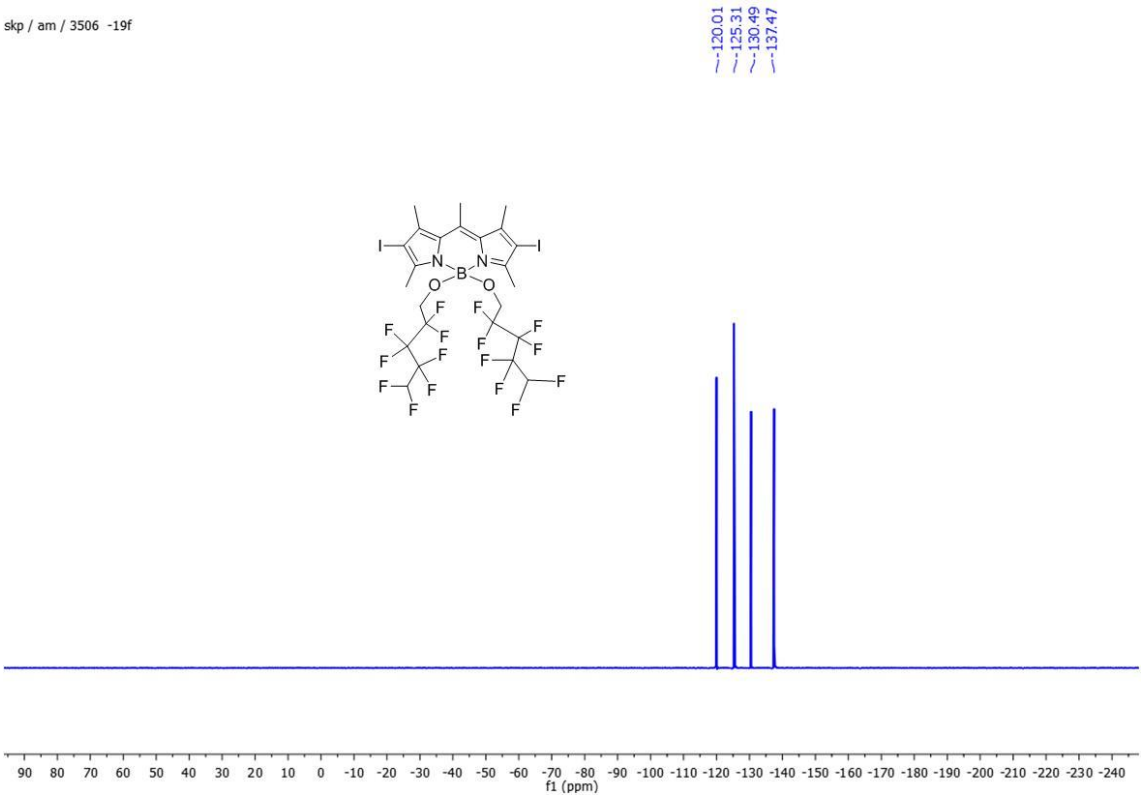


Fig S2b: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3**.

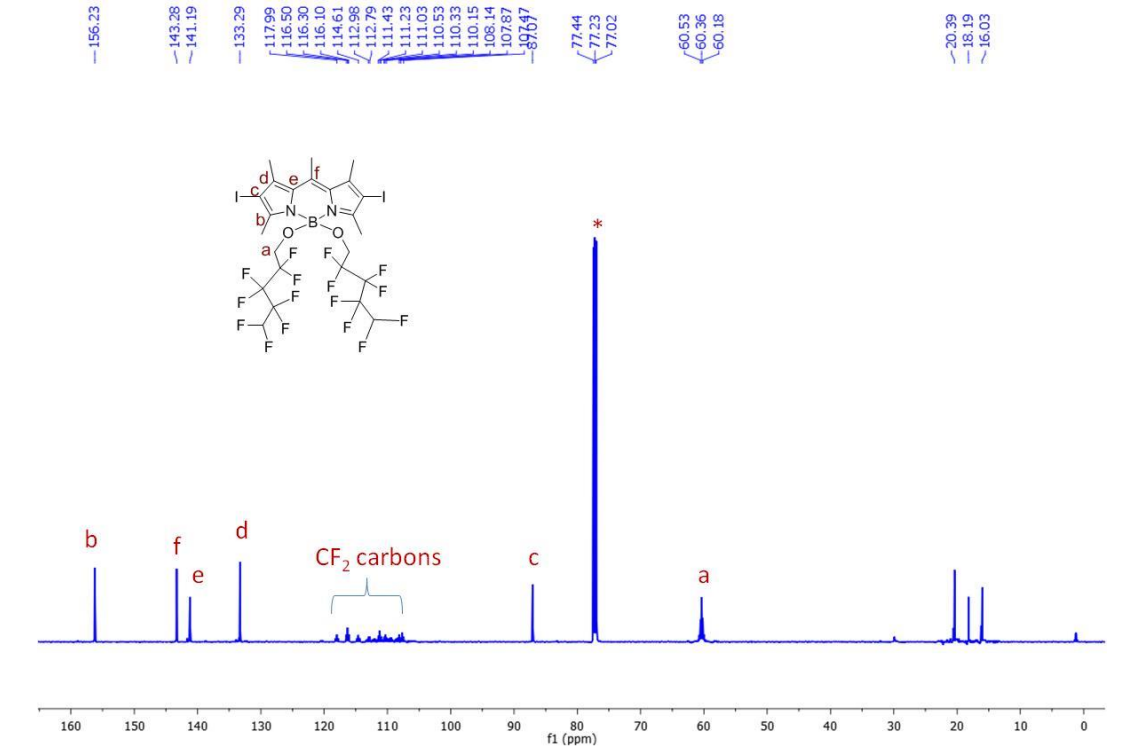


Fig S2c: $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) spectrum of **3**.

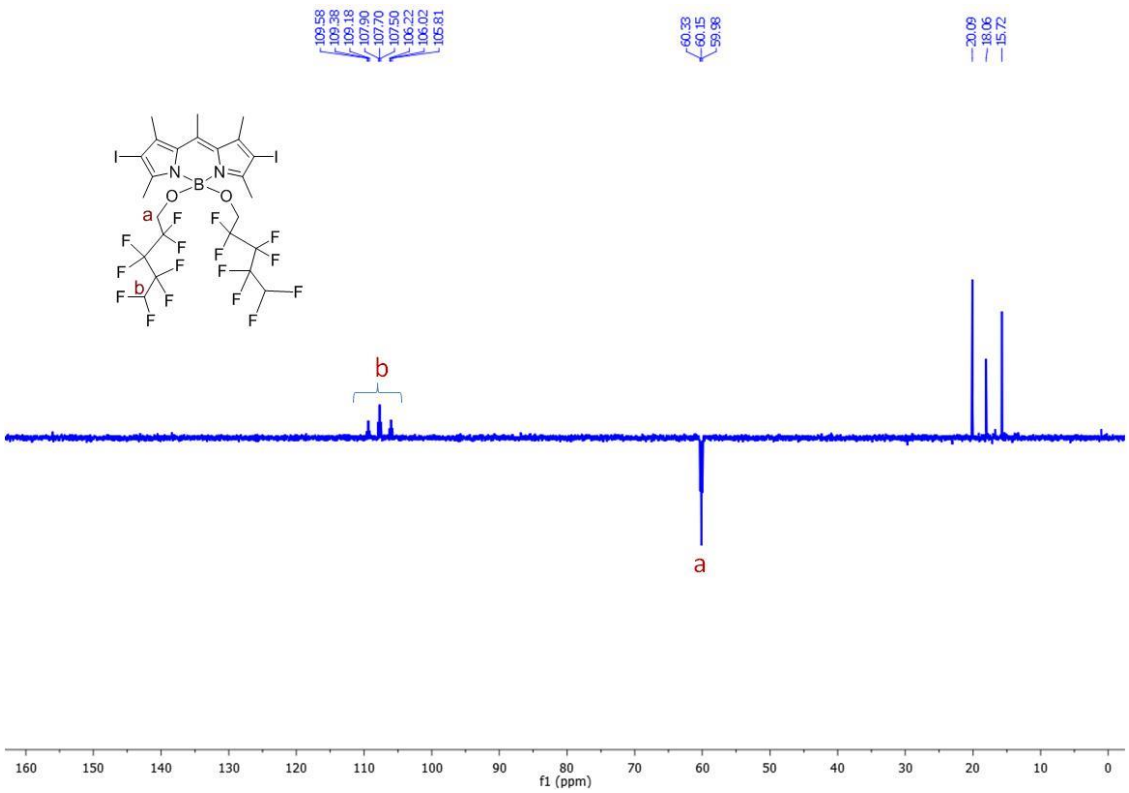


Fig S2d: DEPT-135 NMR (150 MHz, $CDCl_3$) spectrum of **3**.

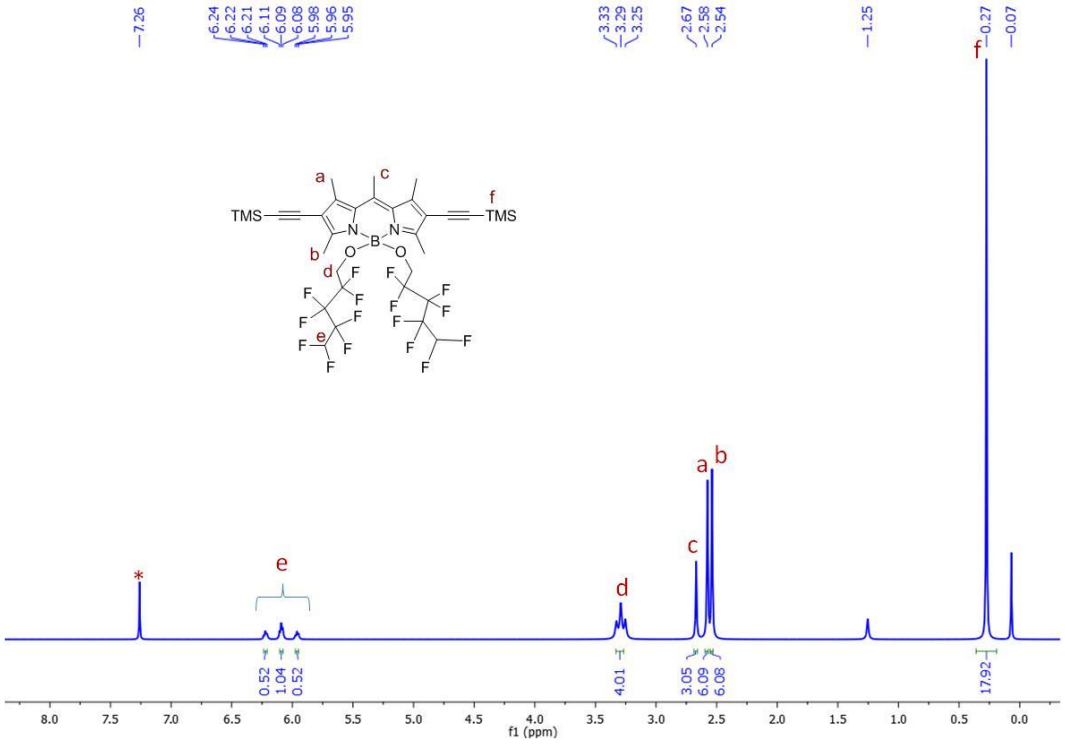


Fig S3a: ^1H NMR (400 MHz, $CDCl_3$) spectrum of **4**.

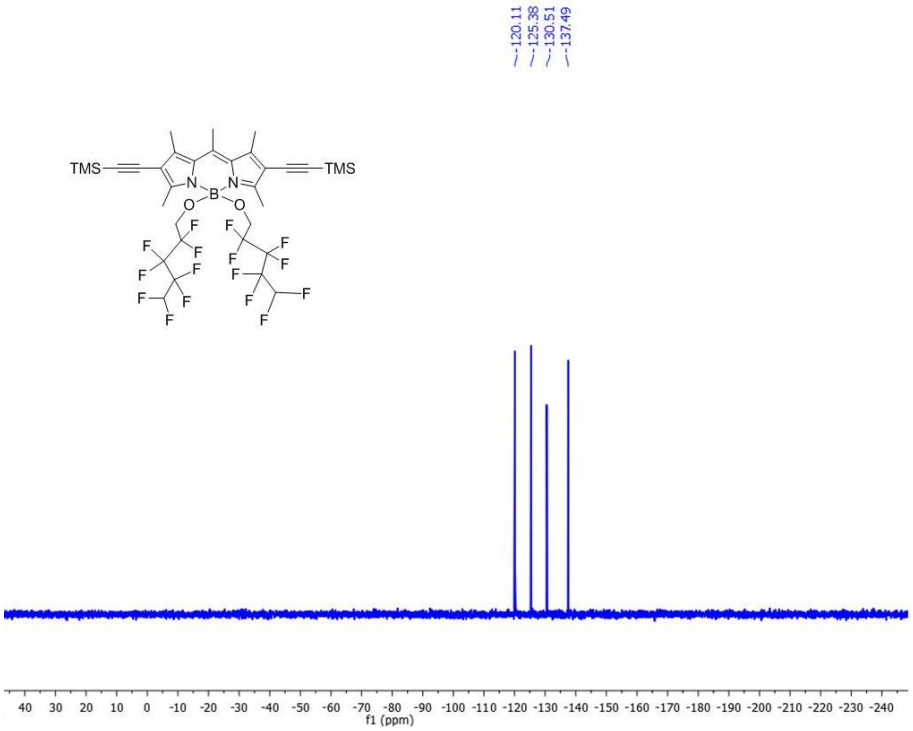


Fig S3b: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **4**.

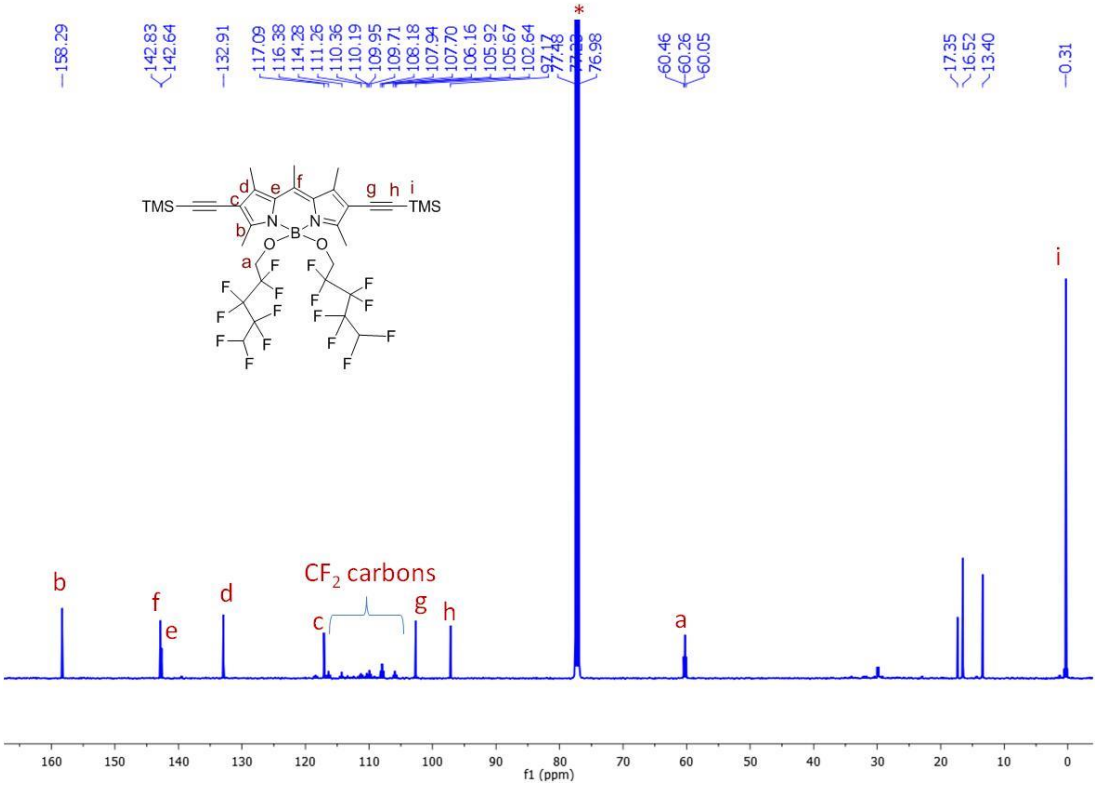


Fig S3c: $^{13}C\{^{1}H\}$NMR (125 MHz, $CDCl_3$) spectrum of **4**.

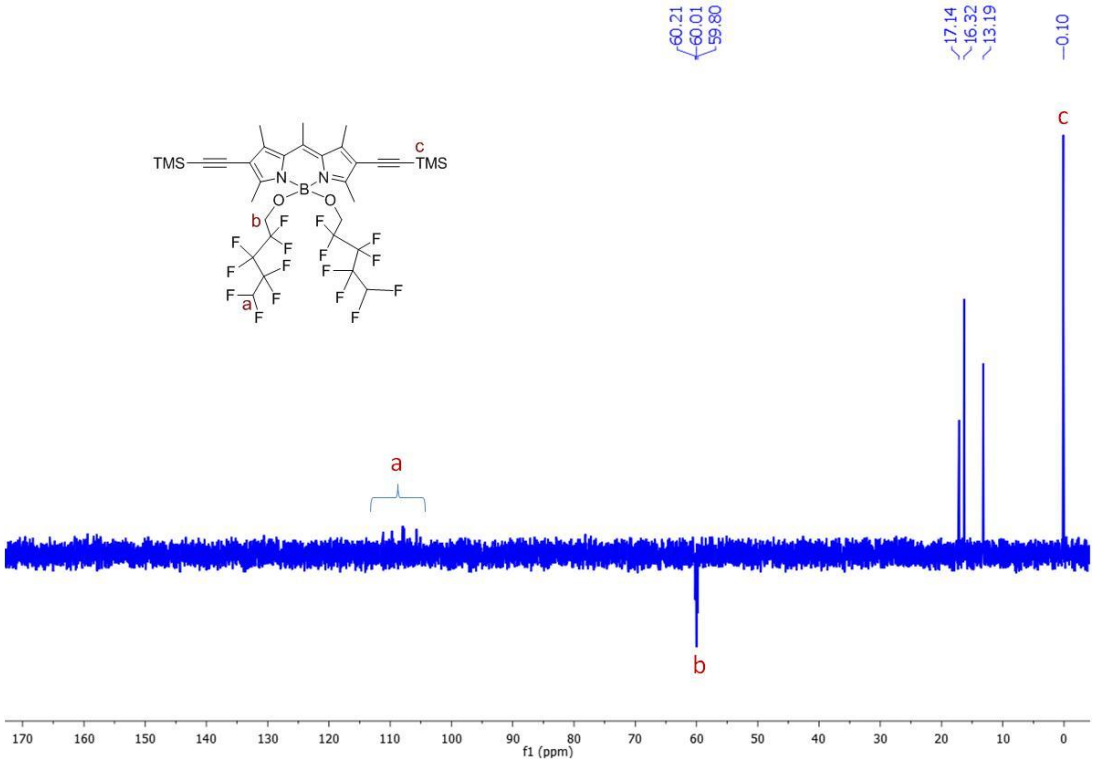


Fig S3d: DEPT-135 NMR (125 MHz, $CDCl_3$) spectrum of **4**.

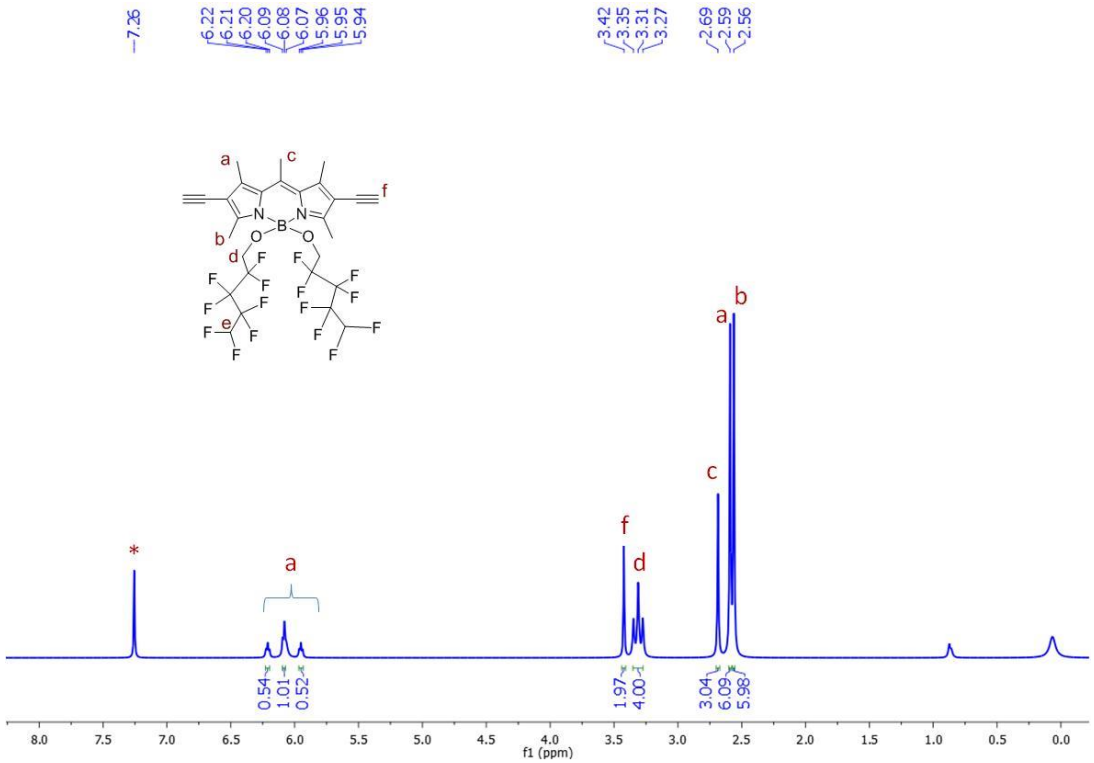


Fig S4a: ^1H NMR (400 MHz, $CDCl_3$) spectrum of **FBDP1**.

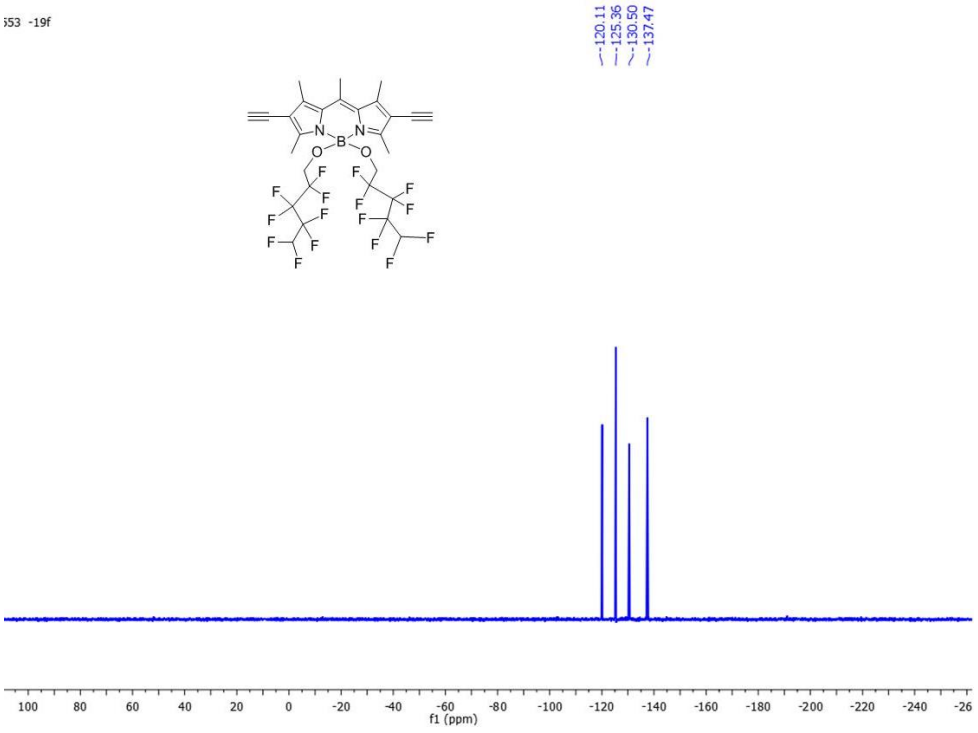


Fig S4b: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **FBDP1**.

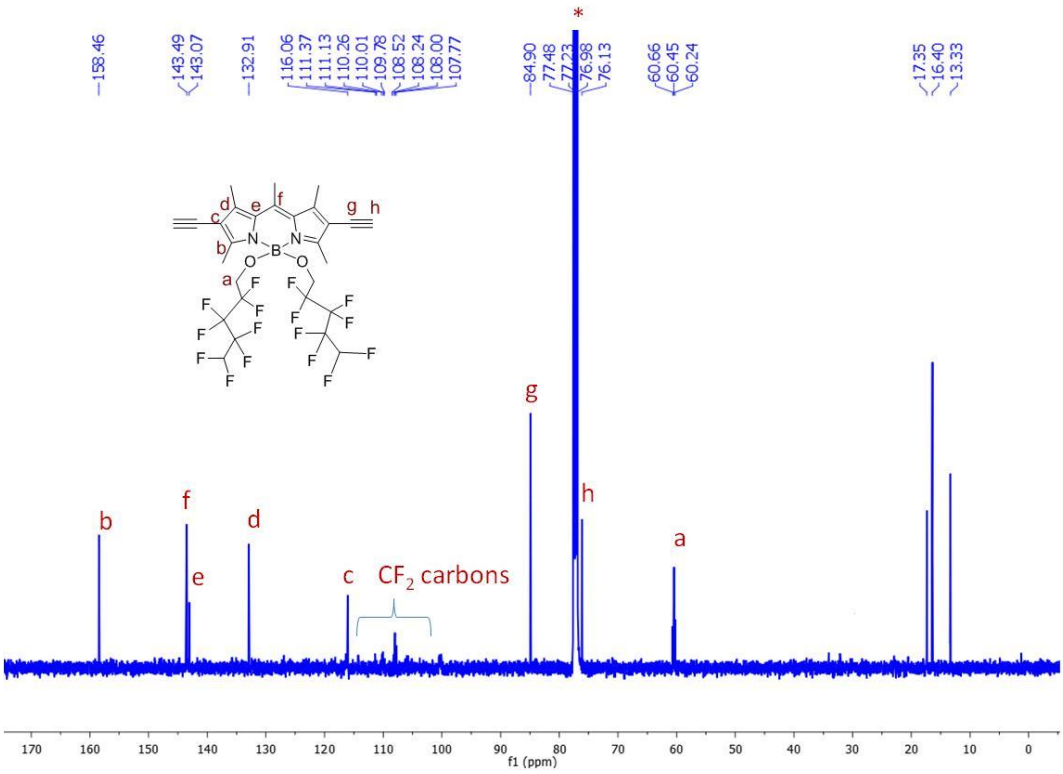


Fig S4c: $^{13}C\{^{1}H\}$NMR (125 MHz, $CDCl_3$) spectrum of **FBDP1**.

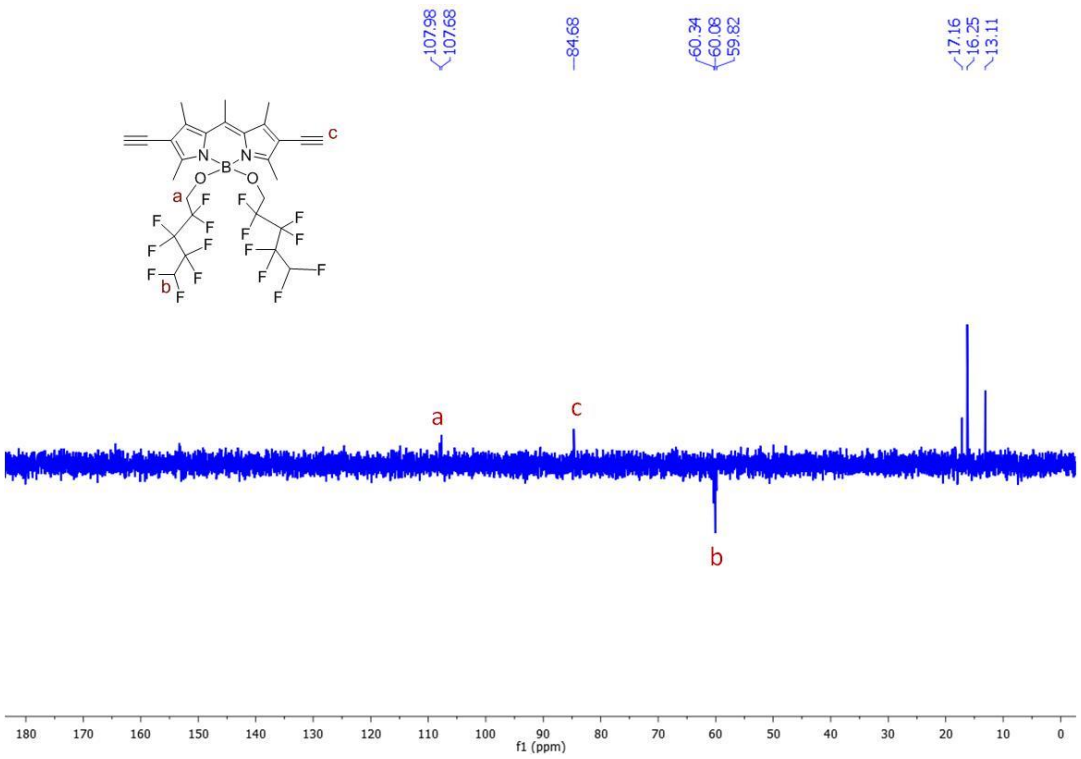


Fig S4d: DEPT-135 NMR (125 MHz, $CDCl_3$) spectrum of **FBDP1**.

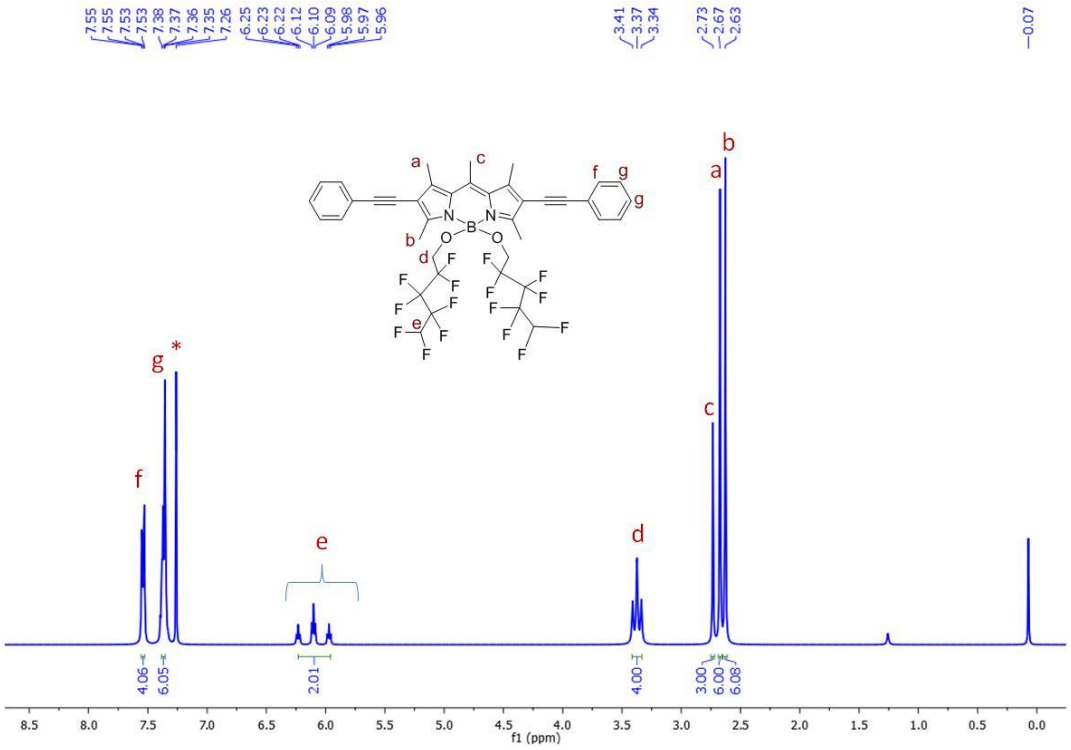


Fig S5a: ^1H NMR (400 MHz, $CDCl_3$) spectrum of **FBDP2**.

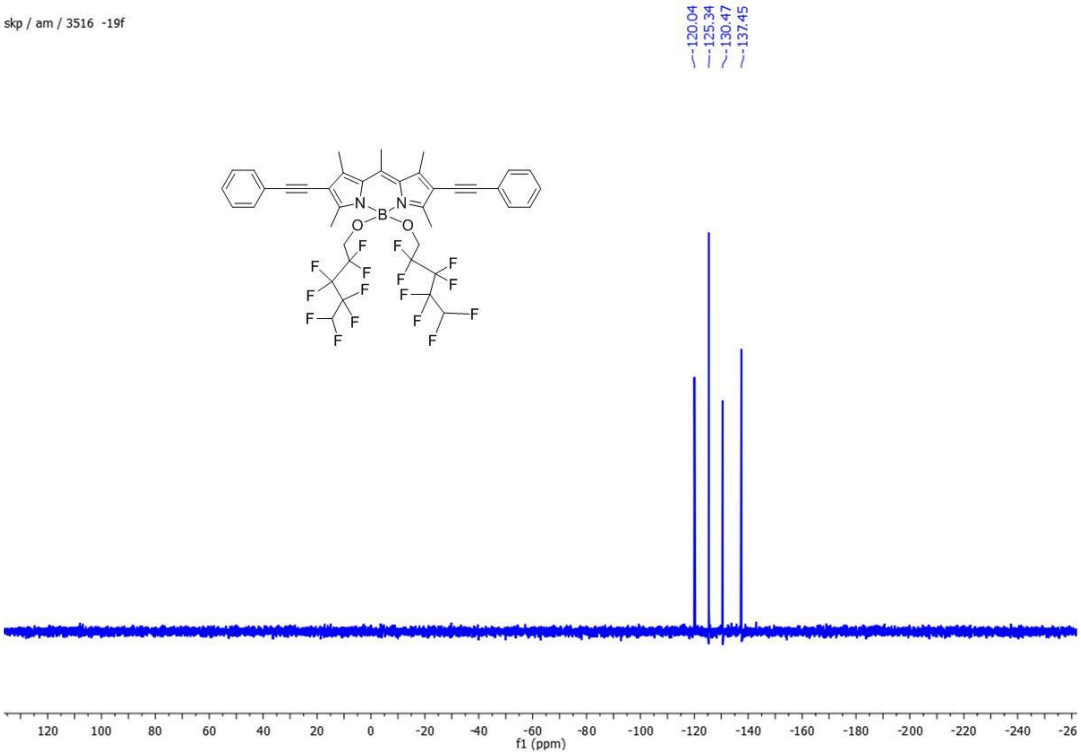


Fig S5b: $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **FBDP2**.

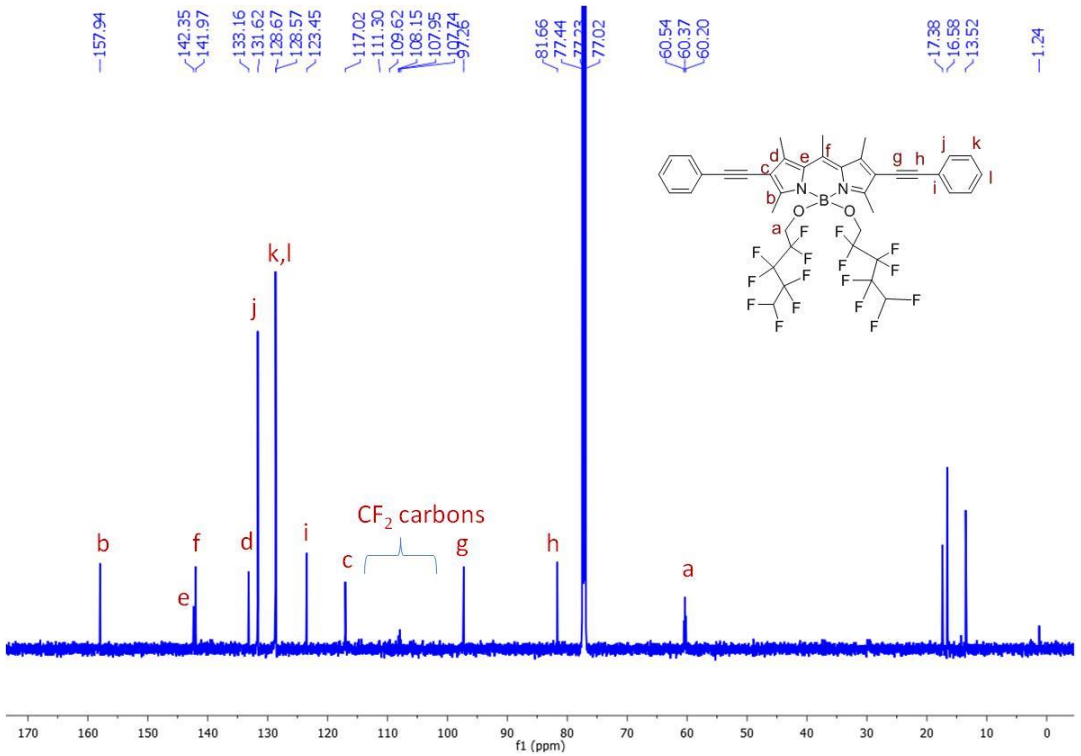


Fig S5c: $^{13}C\{^{1}H\}$NMR (150 MHz, $CDCl_3$) spectrum of **FBDP2**.

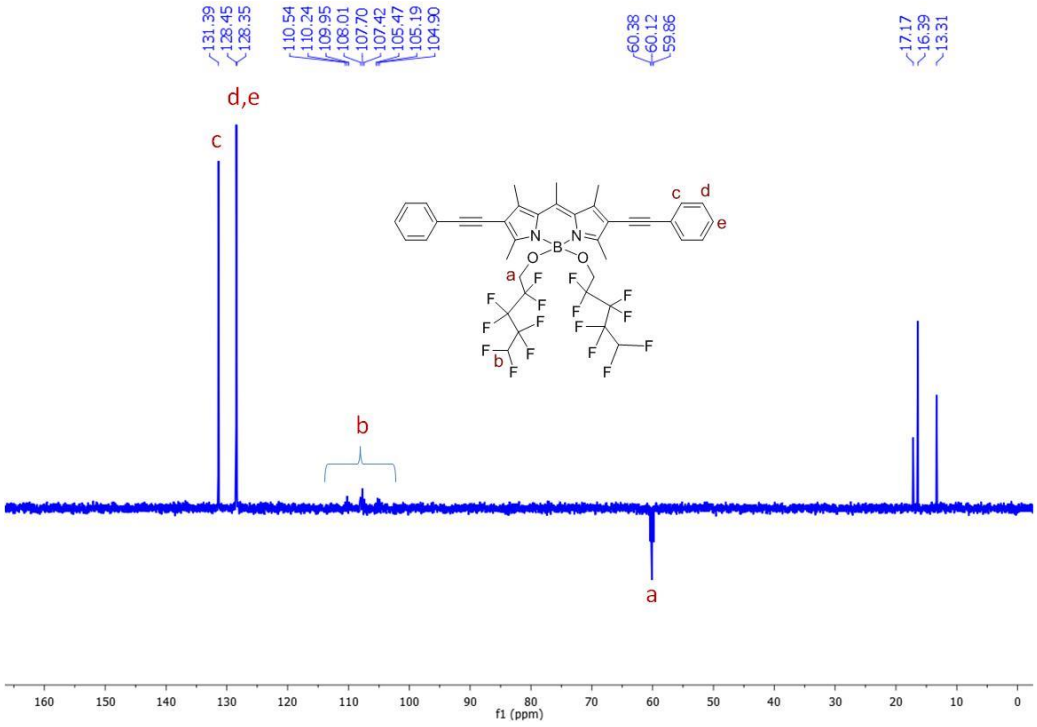


Fig S5d: DEPT-135 NMR (150 MHz, $CDCl_3$) spectrum of **FBDP2**.

1.d) Mass Spectrometric Data

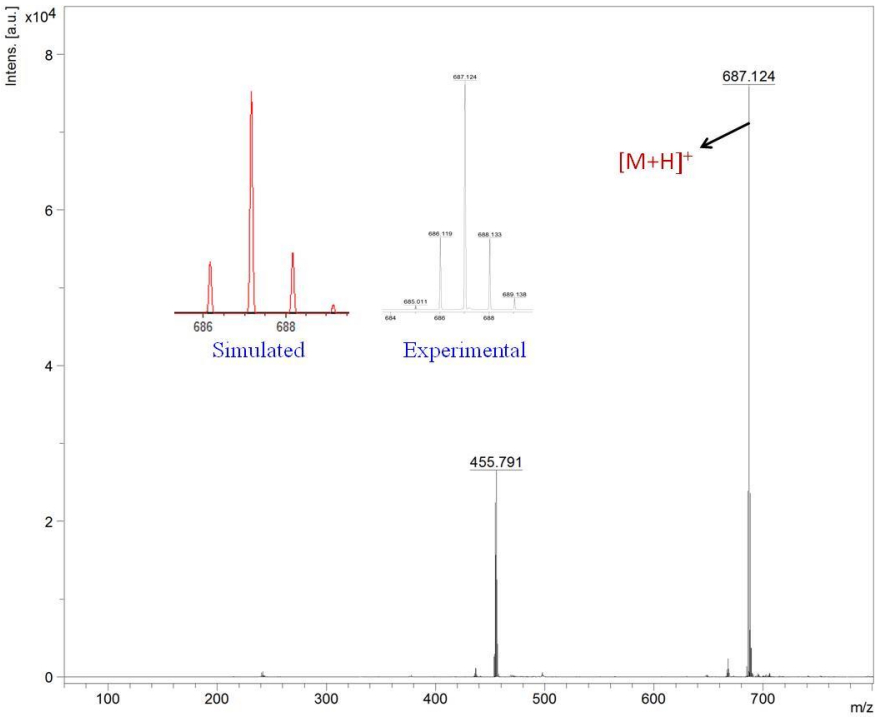


Fig S6: MALDI-TOF mass spectrometry of **2**.

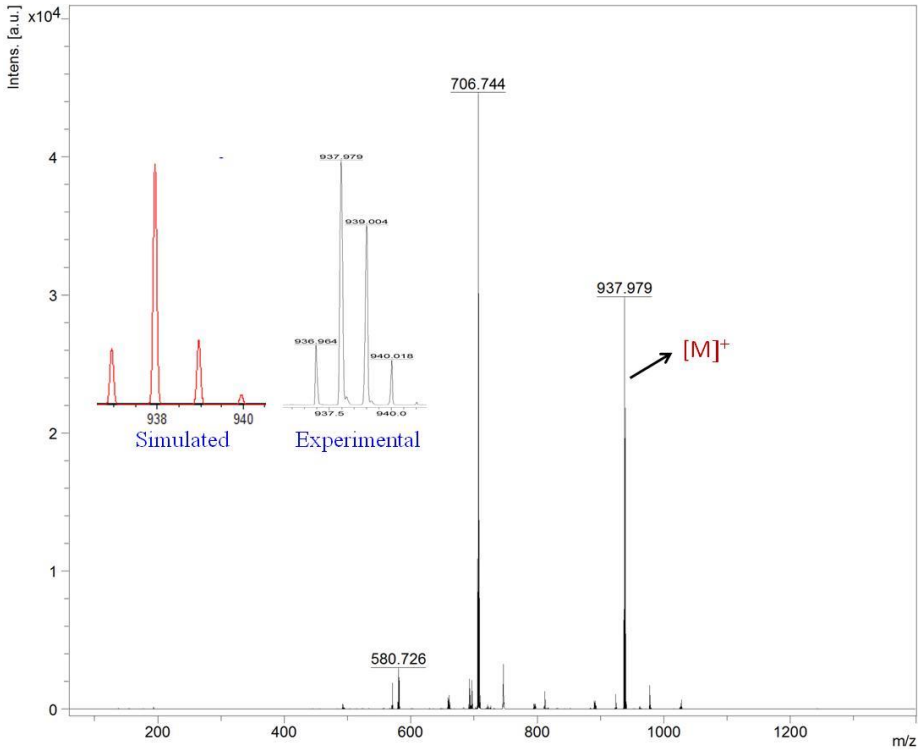


Fig S7: MALDI-TOF mass spectrometry of **3**

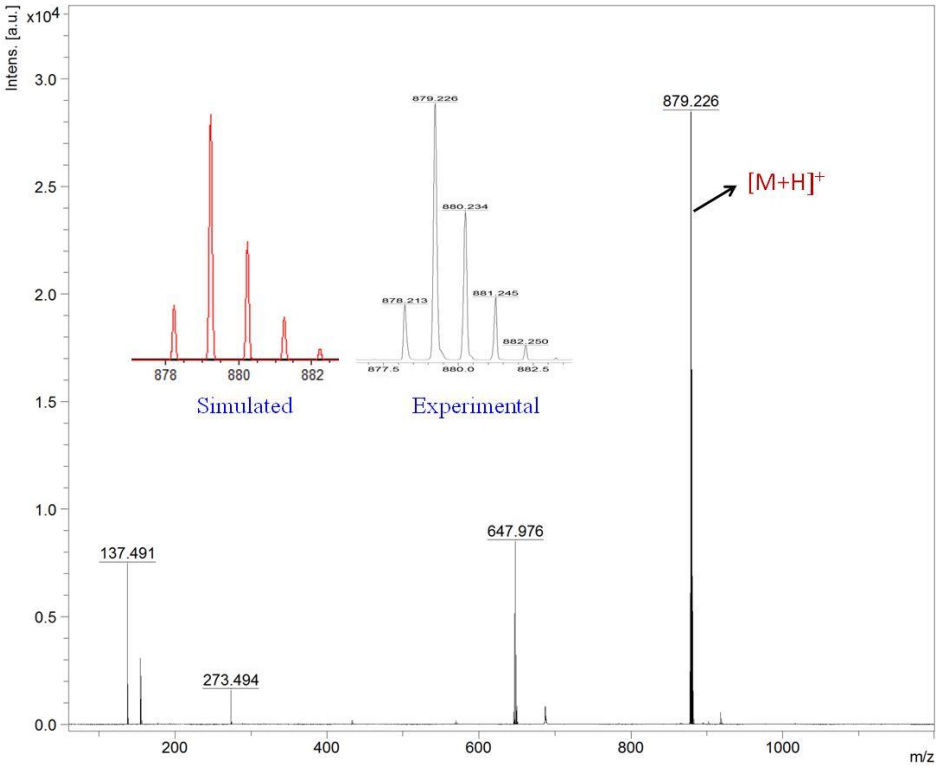


Fig S8: MALDI-TOF mass spectrometry of **4**.

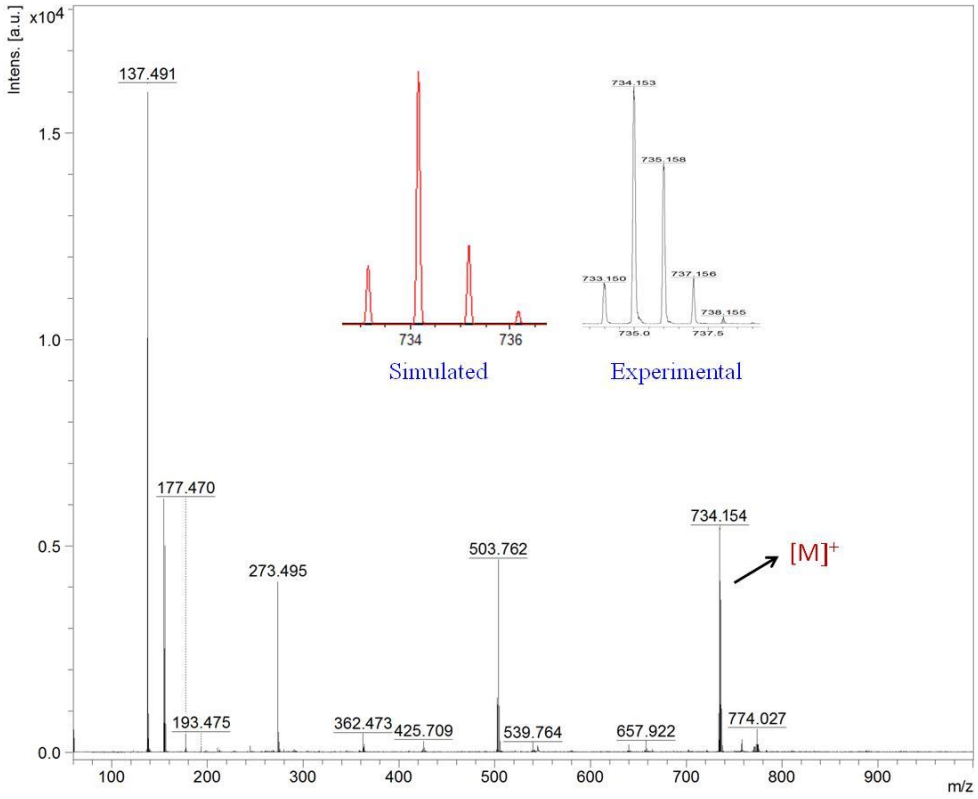


Fig S9: MALDI-TOF mass spectrometry of **FBDP1**.

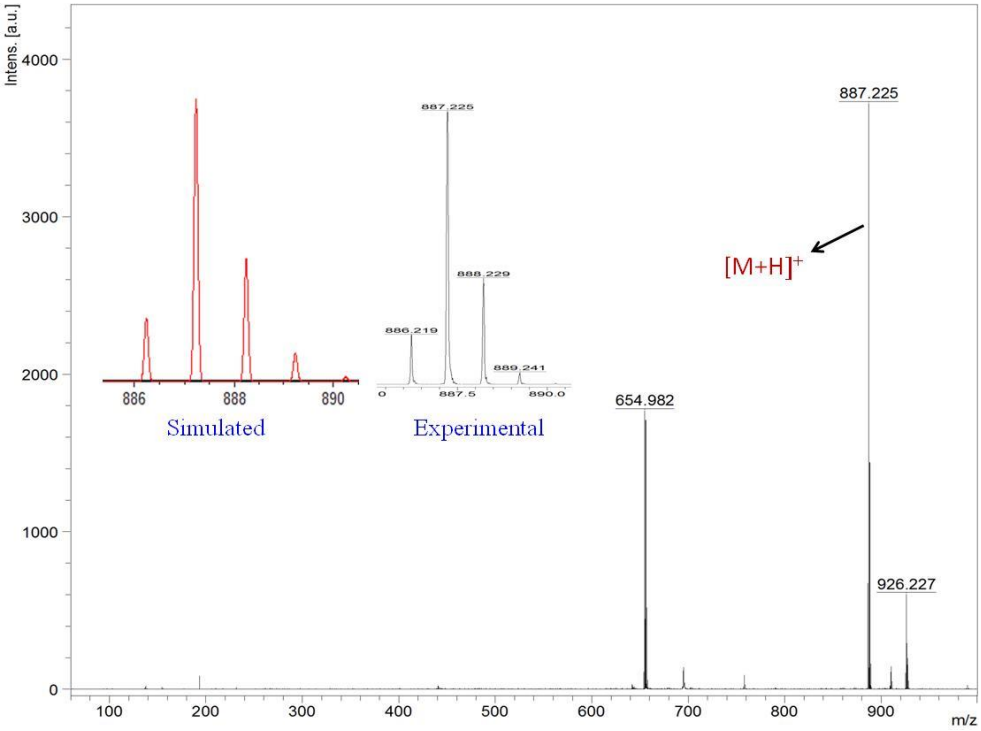


Fig S10: MALDI-TOF mass spectrometry of **FBDP2**.

1.e) Molecular structure of 3 obtained from Single Crystal X-ray diffraction

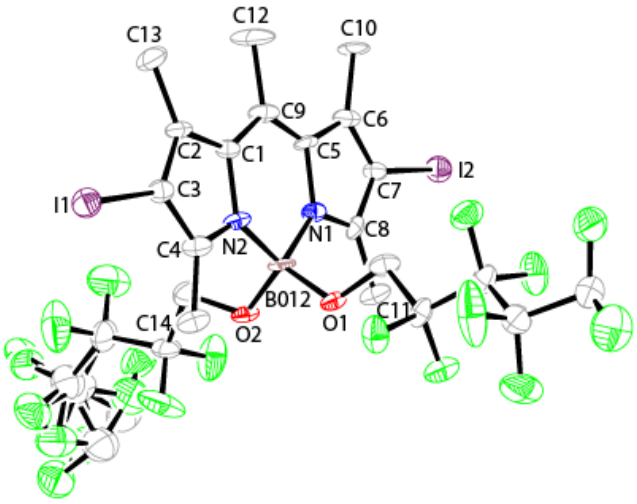


Fig S11: ORTEP representation of compound **3** with hydrogen atoms omitted for clarity. The thermal ellipsoids are drawn at 40% of probability.

2. Photophysical study

2a. Determination of Quantum yield:

All the UV−Vis absorption and fluorescence emission spectra were collected using a Shimadzu UV−Vis spectrophotometer (model UV 2450) and a Spex Fluorolog-3 spectrofluorimeter (model FL3−11) respectively. Throughout all the measurements, the concentration were maintained at (1×10^{-5}) M. Fluorescence quantum yields were measured with respect to a secondary standard fluorescein in 0.1 M NaOH ($\Phi = 0.79$) at 298 K.[6] The sample and standard concentrations were adjusted to obtain an absorbance of 0.1 or less. The following equation was used to calculate the quantum yields:[7]

$$\frac{\boldsymbol{\Phi_S}}{\boldsymbol{\Phi_R}} = \frac{\boldsymbol{A_S}}{\boldsymbol{A_R}} \times \frac{(\boldsymbol{Abs})_{\boldsymbol{R}}}{(\boldsymbol{Abs})_{\boldsymbol{S}}} \times \frac{\boldsymbol{\eta_S^2}}{\boldsymbol{\eta_R^2}}$$

Here Φ represents the quantum yield, (Abs) represents the absorbance, A represents the area under the fluorescence curve, and η is the refractive index of solvents. The subscript S and R denote the corresponding parameters for the sample and reference respectively.

2b. Preparation of thin film for solid state absorption measurement:

The quartz substrates (17 x 15 x 1 mm^3) were cleaned in a fresh piranha solution (7:3 mixture of 98% H_2SO_4 and 30% H_2O_2), washed with Milli-Q water, and followed by

ultrasonication in alkaline isopropanol and 0.1 M aqueous HCl at 60 ˚C for 1 h each. After careful washing with Milli-Q water, thin films of the compounds were prepared by spin coating on quartz plate. A solution of BODIPY dyes in chloroform (~10^{-3} M) was dropped on quartz plate and it was spin coated at 5000 rpm for 60 second followed by 8000 rpm for 120 seconds.

2c. Photophysical study of FBDP2 in various solvents

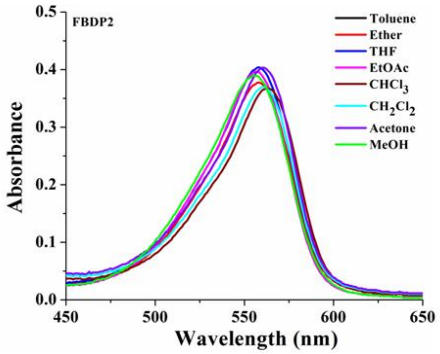


Fig S12: Absorbance spectra of **FBDP2** in different solvents at 1×10^{-5} M concentration.

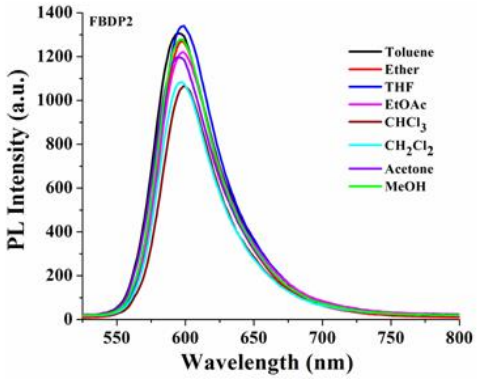


Fig S13: Emission spectra of **FBDP2** in different solvents at 1×10^{-5} M concentration.

2d. Determining 0-0 transition energy from absorption and fluorescence spectra:

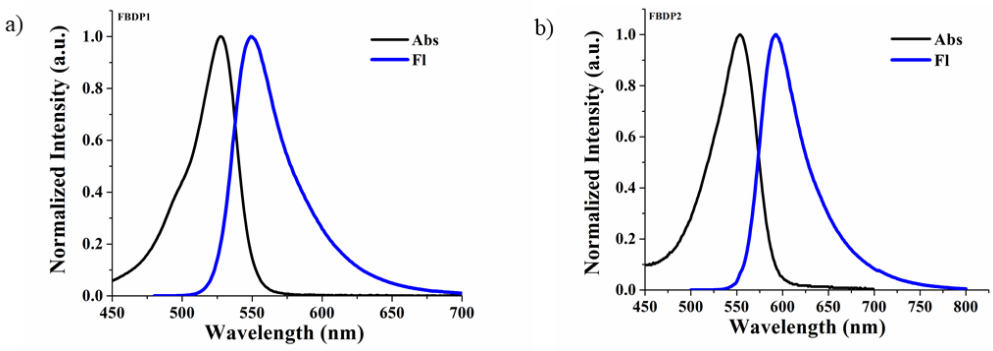


Figure S14: Normalized absorption and emission spectra of **FBDP1-2** in solution (MeOH) for determining 0-0 transition energy. Intersection wavelength are 537.8 and 573.5 nm respectively.

2e. Photophysical tables:

Table S1 Photophysical parameters of **FBDP1**

Solvent	$E_T(30)$[a]	λ_{abs} (nm)	ε_{max}[b] × 10^4 ($M^{-1}cm^{-1}$)	λ_{em} (nm)	$\Delta\upsilon_{st}$[c] (cm^{-1})	FWHM (cm^{-1})	φ_F[d]	$\varepsilon_{max}\times\varphi_F$ ($M^{-1}cm^{-1}$)
Toluene	33.9	529	4.4	557	950	1307	0.65	2.86
Ether	34.5	530	4.5	554	817	1235	0.58	2.61
THF	37.4	531	4.2	556	847	1187	0.63	2.65
EtOAc	38.1	529	3.8	553	820	1235	0.48	1.82
$CHCl_3$	39.1	534	4.0	554	676	1069	0.64	2.56
CH_2Cl_2	40.7	532	4.3	556	811	1093	0.66	2.84
Acetone	42.2	527	3.9	551	827	1323	0.43	1.68
MeOH	55.5	530	4.1	555	849	1273	0.72	2.95

Table S2 Photophysical parameters of **FBDP2**

Solvent	$E_T(30)$[a]	λ_{abs} (nm)	ε_{max}[b] × 10^4 ($M^{-1}cm^{-1}$)	λ_{em} (nm)	$\Delta\upsilon_{st}$ (cm^{-1})	FWHM (cm^{-1})	φ_F[d]	$\varepsilon_{max}\times\varphi_F$ ($M^{-1}cm^{-1}$)
Toluene	33.9	562	3.8	595	987	1473	0.37	1.41
Ether	34.5	557	3.7	597	1203	1327	0.35	1.29
THF	37.4	558	4.0	598	1199	1378	0.56	2.24
EtOAc	38.1	556	3.9	597	1235	1458	0.54	2.11
$CHCl_3$	39.1	562	3.6	598	1071	1318	0.44	1.58
CH_2Cl_2	40.7	560	3.7	596	1079	1383	0.46	1.70
Acetone	42.2	560	4.0	595	1051	1473	0.47	1.88
MeOH	55.5	555	3.9	596	1240	1387	0.61	2.38

2f. Life time data

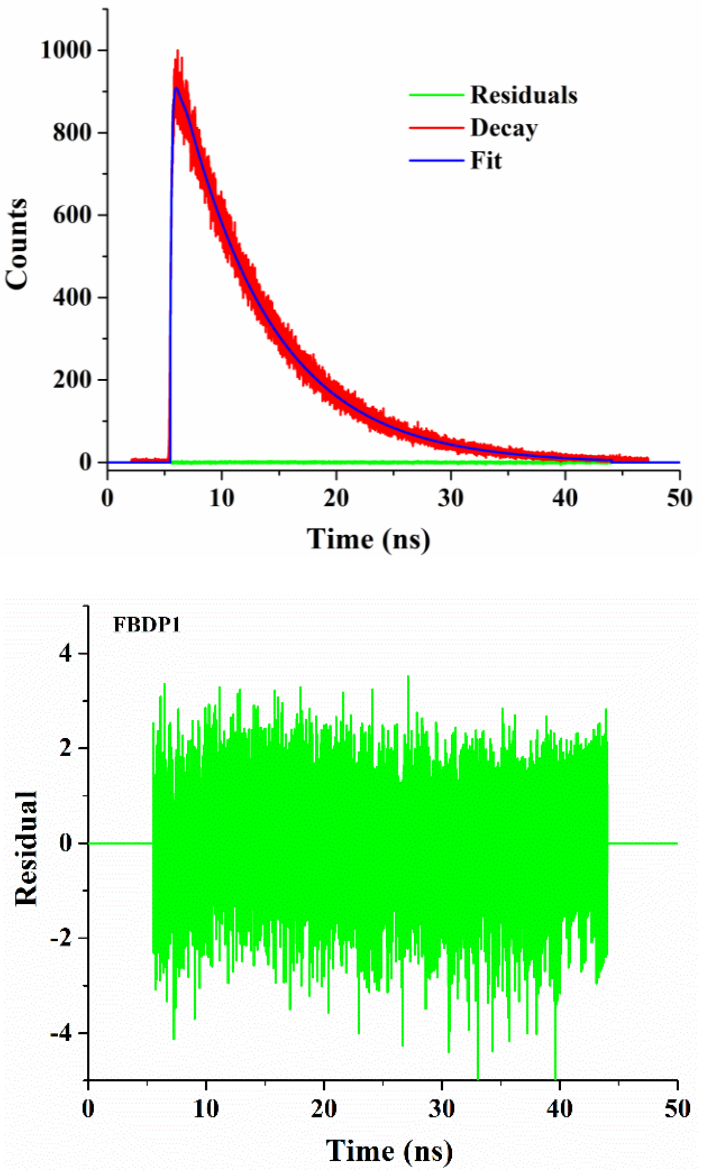


Figure S15: Fluorescence decay curve and the residual plot for **FBDP1**.

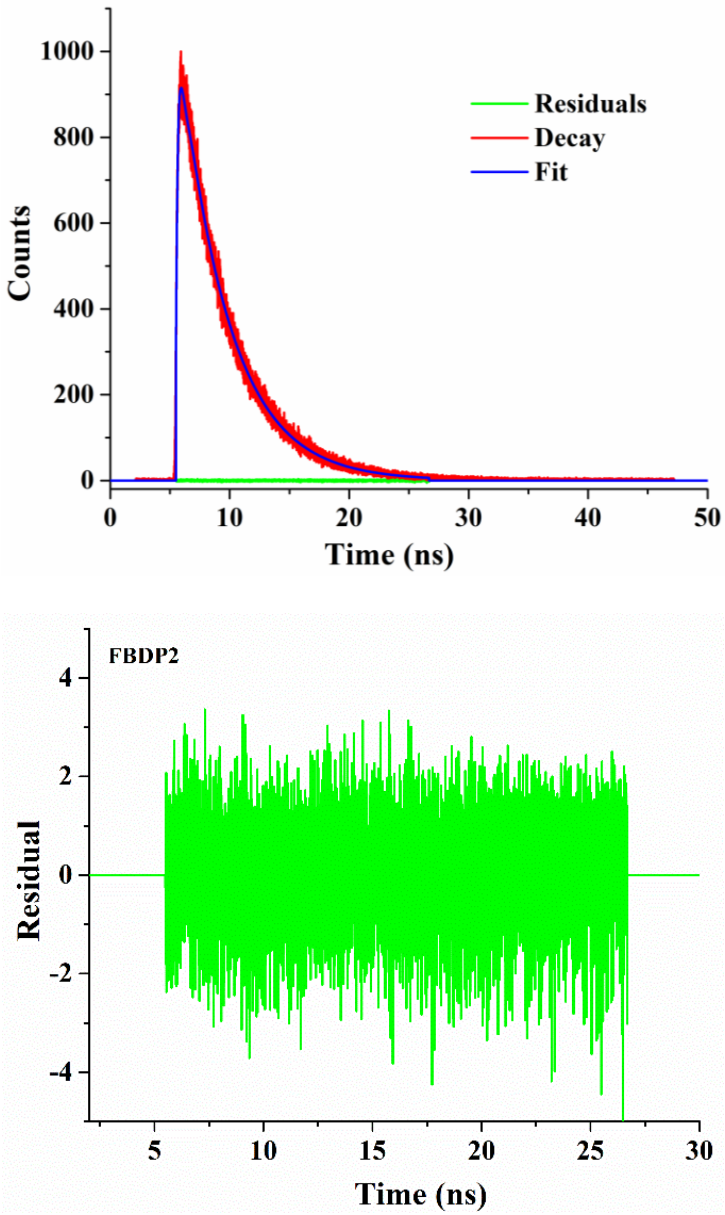


Figure S16: Fluorescence decay curve and the residual plot for **FBDP2**.

3. Device microstructure

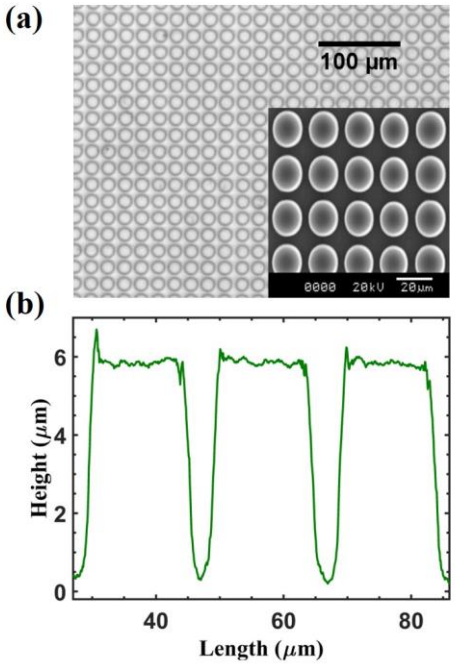


Figure S17: (a) Optical microscope image along with the SEM image (inset) of a part of the square lattice pattern replicated on PDMS polymer. (b) 3-D profilometry depth profile of the PDMS pillars is plotted along an array of the PDMS pillars, wherein the on-average height of the pillars is observed to be 5.48 µm.

4. Random lasing spectra

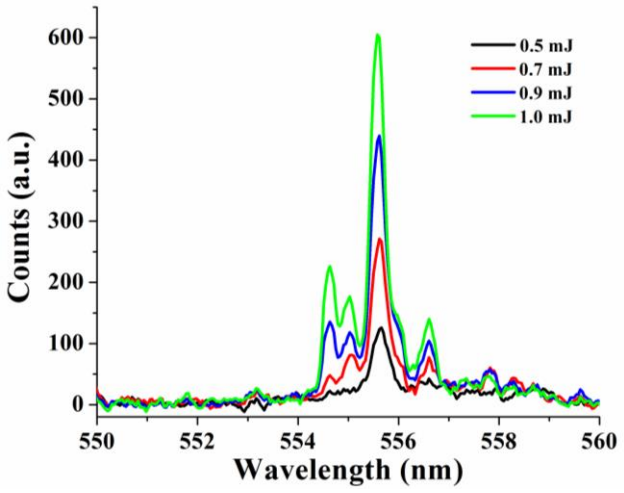


Figure S18: The output random lasing spectra of **FBDP1** with different pump energy in a MFD**.**

5. Crystallographic data

Table S3 Crystallographic data and refinement parameters for compound **3** and **FBDP2.** Data were collected at 293 K.

	3	**FBDP2**
Empirical formula	$C_{24}H_{21}BF_{16}I_2N_2O_2$	$C_{40}H_{31}BF_{16}N_2O_2$
Formula weight	938.04	886.503
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$
a, Å	16.1767(9)	12.1085(10)
b, Å	8.7841(5)	13.8332(11)
c, Å	21.7797(12)	13.9870(11)
α, deg	90	119.059(2)
β, deg	90	101.268(2)
γ, deg	90	94.837(2)
V, Å^3	3094.8(3)	1964.0(3)
Z	4	2
ρ_{calcd}, g cm^{-3}	2.013	1.499
μ, mm^{-1}	2.156	0.144
F(000)	1800	900
Reflections		
Collected	7404	25508
independent	5876	8463
Observed [$I > 2\sigma(I)$]	5288	6212
No. of variables	484	555
Goodness-of-fit	1.039	1.047
Final R indices [$I>2\sigma(I)$][a]	R_1 = 0.0478	0.0550
	wR_2 = 0.1024	0.1380
R indices (all data)[a]	R_1 = 0.0544	0.0755
	wR_2 = 0.1054	0.1486

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma|F_o^2|^2$.

Table S4. Important bond lengths and bond angles in compounds **3** and **FBDP2**.

3		**FBDP2**	
Bond Distances (A˚)			
C7-I2	2.071(12)	C2-C6	1.499(3)
C3-I1	2.081(13)	C15-C16	1.497(3)
N2-B1	1.569(16)	C18-C22	1.491(4)
N1-B1	1.592(16)	C7-C8	1.197(4)
B1-O1	1.443(16)	C23-C24	1.200(4)
B1-O2	1.431(16)	N2-B1	1.566(3)
		N1-B1	1.576(3)
		B1-O1	1.437(3)
		B1-O2	1.442(3)
Bond Angles (˚)			
C4-C3-I1	123.2(9)	C2-C3-C7	127.8(2)
C2-C3-I1	126.3(9)	C4-C3-C7	123.7(3)
C6-C7-I2	126.2(9)	C18-C19-C23	126.1(2)
C8-C7-I2	124.9(9)	C20-C19-C23	125.8(2)
O1-B1-O2	105.2(8)	O1-B1-O2	104.67(19)
O2-B1-N1	112.0(10)	O2-B1-N1	110.7(2)
O2-B1-N2	113.3(11)	O2-B1-N2	111.1(2)
O1-B1-N2	112.1(10)	O1-B1-N2	113.7(2)
O1-B1-N1	109.9(11)	O1-B1-N1	111.8(2)
N1-B1-N2	104.5(8)	N1-B1-N2	105.07(19)
Torsional angle (˚)			
-	-	C10-C9-C3-C2	8.85
-	-	C14-C9-C3-C4	6.90
-	-	C18-C19-C25-C26	-11.15
-	-	C20-C19-C25-C30	-10.68

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