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Boron Dipyrromethene with *meso*-perfluorinated Alkyl Substituents as Near Infrared Donors in Organic Solar Cells

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1. Synthesis and Characterization

All the reactant are commercial available and used as received without further purification. Solvents are used as commercial grade and are not anhydrous unless specially addressed. All the chemical reactions are conducted in nitrogen atmosphere. ^{1}H NMR spectra are recorded on a Bruker DRX 500 P instrument and ^{19}F NMR are recorded on a Bruker Avance 300 instrument. Mass spectra are measured on a Bruker Esquir-LC 00084 instrument in DCM solution. The reactant of the dimerization step, 2-(4-methoxyphenyl)-4*H*-furo[3,2-b]pyrrole-5-carboxylic acid, is synthesized according to the reported method.[1] The obtained reactant is light grey powder, and is completely dried in a vacuum oven.

The general synthetic route of the BODIPY precursors **preBDP1-preBDP-3** is exactly the same. The anhydrous 2-(4-methoxyphenyl)-4*H*-furo[3,2-b]pyrrole-5-carboxylic acid (2 mmol, 0.51 g) is added into 30 mL of perfluorinated acid, and heat at 40°C for 10 mins. Then, 6 mL of the corresponding acid anhydride is injected into the mixture dropwise at strong stirring. Heat up the system to refluxing, and intense greenish blue color can be observed. After 1 h, pour the mixture into large amount of cold water and neutralize the solution by sodium carbonate. The raw material is extracted by DCM, and flash column chromatography (silicon, eluent: DCM) is performed to provide the BODIPY precursors.

preBDP-1: trifluoroacetic acid and trifluoroacetic anhydride is used. Dark purple solid, 0.22 g (yield: 45%). ESI-MS calcd. *m/z* 505.4 for $[C_{28}H_{20}F_3N_2O_4]^+$, found 505.1. ^{1}H NMR (500 MHz, $CDCl_3$) δ 13.33 (s, 1H), 7.75–7.71 (m, 4H), 6.98–6.93 (m, 4H), 6.66–6.63 (m, 2H), 6.52 (d, *J*=0.8 Hz, 2H), 3.86 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -53.02 (s).

preBDP-2: pentafluoropropionic acid and pentafluoropropionic anhydride is used. Dark purple solid, 0.23 g (yield: 42%). ESI-MS calcd. *m/z* 555.1 for $[C_{29}H_{20}F_5N_2O_4]^+$, found 555.3. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J*=8.9 Hz, 4H), 6.90 (d, *J*=8.9 Hz, 4H), 6.51 (s, 2H), 6.46 (s, 2H), 3.81 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -53.03 (s), -69.09 (s).

preBDP-3: heptafluorobutyric acid and heptafluorobutyric anhydride is used. Dark purple solid, 0.24 g (yield: 40%). ESI-MS calcd. *m/z* 605.1 for $[C_{30}H_{20}F_7N_2O_4]^+$, found 605.3. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72–7.63 (m, 4H), 6.96–6.84 (m, 4H), 6.48 (s, 2H), 6.46 (s, 2H), 3.81 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -80.41 (t, *J*=10.6 Hz), -99.39 (q, *J*=10.3 Hz), -124.11– -124.89 (m).

The synthesis of the BODIPY is carried out according to the well-established method.[2] The precursors (1 mmol) are dissolved in ~200 mL anhydrous DCM at room temperature and the organic base DIPEA (15 mmol, 1.9 g, 2.6 mL) is added into the solution dropwise. The mixture is stirred at room temperature for 1 h. Then, boron trifluoride etherate (15 mmol, 2.1 g, 1.9 mL) is added dropwise and the color change from intense blue to green can be observed. After stirring at room temperature for another 1 h, the solution is poured into large amount of water and extracted by DCM. Flash column chromatography (silicon, eluent: DCM) is performed to provide the final BODIPY product.

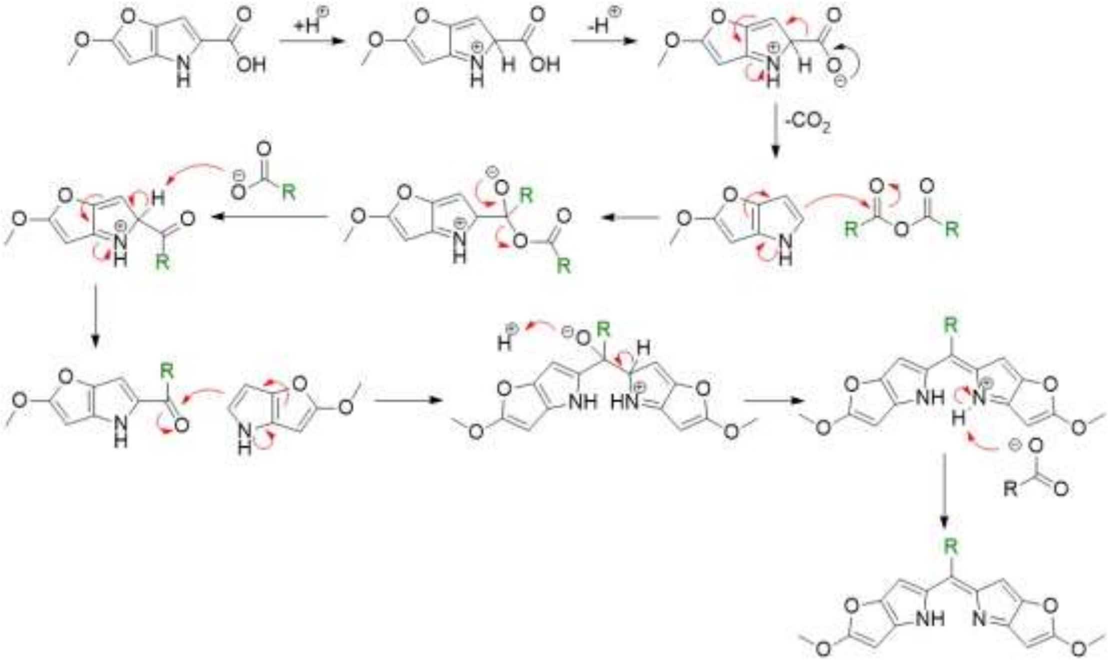
BDP-1: dark green solid, 0.34 g (yield: 62%). ESI-MS calcd. *m/z* 533.2 for $[C_{28}H_{18}BF_4N_2O_4]^+$, found 533.1. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, *J*=8.9 Hz, 4H), 6.93 (d, *J*=9.0 Hz, 4H), 6.75 (s, 2H), 6.66 (s, 2H), 3.83 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -55.06 (s), -149.49 (dd, *J*=56.9, 28.0 Hz).

BDP-2: dark purple solid, 0.4 g (yield: 69%). ESI-MS calcd. *m/z* 583.1 for $[C_{29}H_{18}BF_6N_2O_4]^+$, found 583.3. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77–7.65 (m, 4H), 6.99–6.88 (m, 4H), 6.74 (s, 2H), 6.58 (s, 2H), 3.82 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -84.19 (t, *J*=2.6 Hz), -105.91 (d, *J*=2.6

Hz), -149.48 (dd, *J*=56.5, 28.0 Hz).

BDP-3: dark purple solid, 0.4 g (yield: 63%). ESI-MS calcd. *m/z* 633.1 for $[C_{30}H_{18}BF_8N_2O_4]^+$, found 633.2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.75 (m, 4H), 7.04–6.95 (m, 4H), 6.81 (s, 2H), 6.62 (s, 2H), 3.88 (s, 6H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.68 (d, *J*=10.5 Hz), -102.04 (d, *J*=10.9 Hz), -124.44 (s), -148.91 (dd, *J*=56.2, 27.8 Hz).

Scheme S1. Proposed dimerization reaction mechanism for the BODIPY precursors

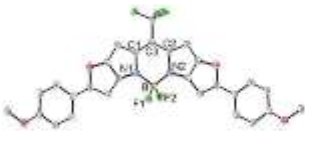
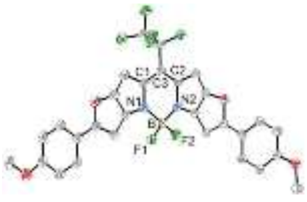
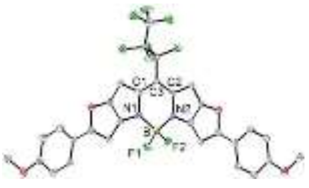


2. Single Crystal Data

Table S1. Crystal data and structure refinement of the BODIPYs

Compound	**BDP-1**	**BDP-2**	**BDP-3**
Empirical formula	$C_{28}H_{18}BF_5N_2O_4$	$C_{29}H_{18}BF_7N_2O_4$	$C_{30}H_{18}BF_9N_2O_4$
Formula weight	552.25	602.26	652.27
Temperature/K	100.0(2)	100.0(2)	100.0(3)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.4718(5)	7.6728(3)	11.7774(4)
b [Å]	9.4932(3)	12.6770(6)	15.2002(4)
c [Å]	13.4657(3)	13.41465(19)	17.0421(4)
α [°]	91.530(2)	102.618(3)	93.918(2)
β [°]	91.845(3)	90.338(2)	105.682(3)
γ [°]	108.004(4)	100.899(4)	97.023(3)
Volume [Å^3]	1150.07(8)	1248.82(8)	2898.81(16)
Z	2	2	4
ρ_{calc} [g/cm^3]	1.595	1.602	1.495
μ [mm^{-1}]	1.152	1.235	1.214
F(000)	564.0	612.0	1320.0
Radiation	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)	CuK_α (λ = 1.54184)
2Θ range for data collection [°]	6.572 to 153.382	6.76 to 154.622	5.416 to 153.602
Index ranges	$-11 \leqslant h \leqslant 10$ $-11 \leqslant k \leqslant 11$ $-16 \leqslant l \leqslant 16$	$-9 \leqslant h \leqslant 9$ $-15 \leqslant k \leqslant 15$ $-16 \leqslant l \leqslant 7$	$-13 \leqslant h \leqslant 14$ $-19 \leqslant k \leqslant 19$ $-21 \leqslant l \leqslant 21$
Reflections collected	23344	12670	36690
Independent reflections	4781 [R_{int}=0.0357, R_{sigma}=0.0188]	5192 [R_{int}=0.0236, R_{sigma}=0.0220]	12061 [R_{int}=0.0234, R_{sigma}=0.0252]
Data/restraints/parameters	4781/18/387	5192/0/390	12061/0/833
Goodness-of-fit on F^2	1.188	1.059	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0675, wR_2 = 0.2010	R_1 = 0.0463, wR_2 = 0.1296	R_1 = 0.0392, wR_2 = 0.1173
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.2043	R_1 = 0.0488, wR_2 = 0.1330	R_1 = 0.0472, wR_2 = 0.1234
CCDC No.	1553785	1823943	1823944

Table S2. Selected bond length and bond angles of the BODIPYs

Molecular structure			
Bond length (Å)			
B-F1	1.387(4)	1.3895(19)	1.3854(14)

B-F2	1.399(4)	1.3937(19)	1.3906(14)
B-N1	1.531(4)	1.535(2)	1.5464(15)
B-N2	1.541(4)	1.531(2)	1.5405(15)
N1-C1	1.405(4)	1.4030(19)	1.3999(15)
N2-C2	1.401(4)	1.4040(18)	1.4074(14)
C1-C3	1.407(4)	1.400(2)	1.4040(16)
C2-C3	1.398(4)	1.404(2)	1.3988(16)
Bond angle [°]			
F1-B-F2	108.2(2)	108.97(13)	109.41(10)
N1-B-N2	106.1(2)	105.58(12)	105.15(9)
C1-C3-C2	121.6(3)	121.60(14)	121.51(10)

3. Photophysical and Electrochemical Properties

The molar extinction coefficient is calculated according to the Lambert-Beer law $\varepsilon = A/(b \times c)$, where A is the absorbance, b is the length of the cuvette, and c is the solution concentration. The absorption spectra in solid state are recorded on a Shimadzu SolidSpec-3700 UV-vis-NIR spectrophotometer. All the vacuum-deposited neat film samples have a thickness of 50 nm on quartz substrate. A integrating sphere is used to measure the reflection (R) and the transmission (T) of the film, and the absorption (A) is calculated as $A=1-R-T$. The absorption coefficient is calculated according the equation:

$$\alpha = \frac{1}{d}\ln\left(\frac{1-R}{T}\right)$$

where d is the thickness of the film.

From cyclic voltammetry measurements, the potential is measured using ferrocene as the internal standard ($E_{\mathrm{Fc/Fc+}}=-4.78$ eV). The HOMO/LUMO energy levels are calculated according to the equations:

$$E_{\mathrm{HOMO}} = e\left(V_{\mathrm{sample}}^{\mathrm{ox}} - V_{\mathrm{Fc/Fc^+}}^{\mathrm{ox}}\right) - 4.78\ \mathrm{eV}$$

$$E_{\mathrm{LUMO}} = e\left(V_{\mathrm{sample}}^{\mathrm{red}} - V_{\mathrm{Fc/Fc^+}}^{\mathrm{red}}\right) - 4.78\ \mathrm{eV}$$

where $V_{\mathrm{sample}}^{\mathrm{ox}}/V_{\mathrm{sample}}^{\mathrm{red}}$ and $V_{\mathrm{Fc/Fc^+}}^{\mathrm{ox}}/V_{\mathrm{Fc/Fc^+}}^{\mathrm{red}}$ are the mean value of the cathodic peak potential and anodic peak potential of the sample's redox couples and ferrocene reference redox couple. As shown in Fig S1, the redox couples of BODIPYs in the negative voltage region are obviously dependent on the scan rate. The peaks are partial reversible when the scan rate is low, while they become reversible when the scan rate reaches 400 mV s^{-1} for **BDP-1** and 800 mV s^{-1} for **BDP-2** and **BDP-3**. The HOMO/LUMO energy levels are calculated by the potential from the measurements under high scan rate.

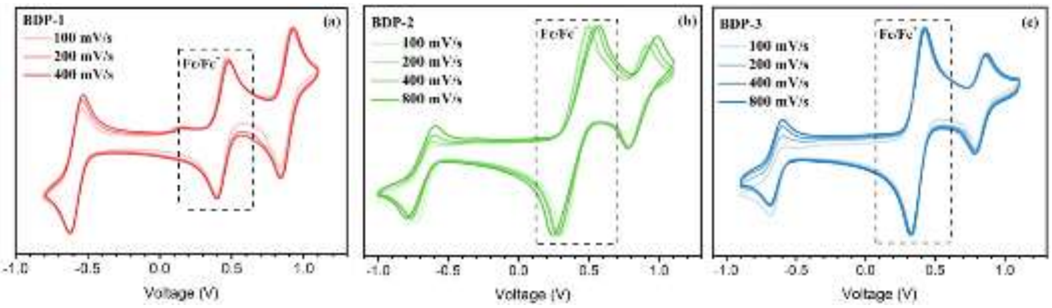


Fig. S1. CV plots of (a) **BDP-1**, (b) **BDP-2** and (c) **BDP-3** at different voltage scan rate in diluted DCM at room temperature. The redox peak from ~0.2 to ~0.6 V is the signal of ferrocene internal reference.

5. Theoretical Calculations

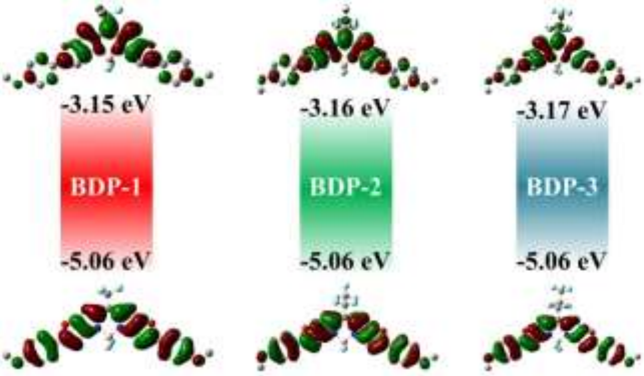


Fig. S2. Calculated HOMO/LUMO plots and the energy levels of the BODIPYs

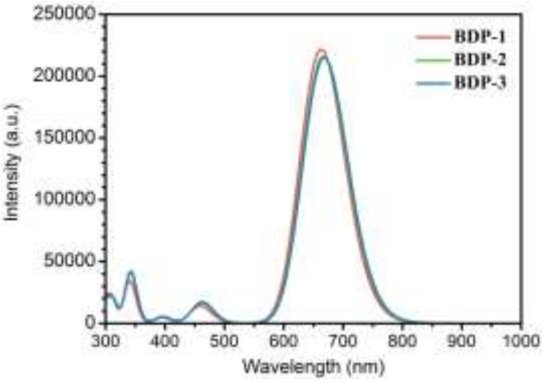


Fig. S3. Simulated UV-vis absorption spectra of the BODIPYs

5. Device fabrication, Characterization and Optimization

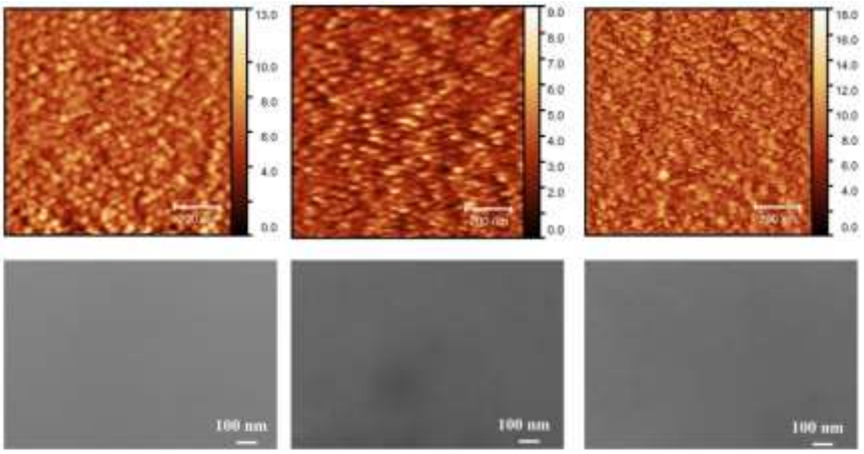
Table S3. Optimization of OSCs with BODIPY NIR donors. Best devices are highlighted in bold.

Donor	Substrate *T* (℃)	BHJ thickness (nm)	j_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
BDP-1	R.T.	30	11.2	0.80	0.47	4.2
	R.T.	40	11.6	0.79	0.44	4.0
	R.T.	50	11.0	0.79	0.44	3.8
	100	30	10.9	0.75	0.68	5.5
	100	40	12.3	0.74	0.66	6.0
	100	**50**	**12.9**	**0.75**	**0.62**	**6.0**
BDP-2	R.T.	30	10.2	0.81	0.43	3.6
	R.T.	40	10.4	0.80	0.43	3.6
	R.T.	50	10.0	0.80	0.44	3.5
	80	40	12.4	0.76	0.59	5.6
	80	45	13.0	0.76	0.59	5.8
	80	50	13.0	0.76	0.55	5.4
	90	40	12.7	0.75	0.62	6.0
	90	45	13.2	0.75	0.61	6.0
	90	50	13.5	0.75	0.59	5.9
	100	40	12.9	0.76	0.65	6.3
	100	45	13.3	0.75	0.63	6.3
	100	50	13.5	0.75	0.61	6.2
	110	40	12.8	0.76	0.65	6.3
	110	45	13.2	0.76	0.64	6.4
	110	**50**	**13.6**	**0.76**	**0.62**	**6.4**
BDP-3	R.T.	30	9.0	0.80	0.45	3.2
	R.T.	40	9.5	0.79	0.45	3.4
	R.T.	50	9.6	0.78	0.46	3.5
	80	40	11.9	0.75	0.58	5.1
	80	45	12.4	0.75	0.57	5.2
	80	50	12.6	0.74	0.55	5.1
	100	30	10.6	0.75	0.68	5.4
	100	40	11.8	0.75	0.65	5.8
	100	50	12.9	0.75	0.61	5.8
	110	40	12.6	0.76	0.63	6.0
	110	45	13.1	0.75	0.62	6.1
	110	**50**	**13.5**	**0.75**	**0.60**	**6.1**

6. Investigation of Morphology and Device Physics

Film samples which resemble the blend active layers in each best-performing device are deposited in a custom-made UHV cluster tool (Bestec, Germany, base pressure < 10^{-8} mbar). The deposition rate is also monitored by quartz crystal monitors. Substrate heating is accomplished using a resistively heated full-area ITO substrate attached to the back of the sample substrate. The temperature is monitored in-situ during the deposition by a thermocouple on the full-ITO substrate connected by silver paste.

Atomic force microscopy (AFM) images are taken on a Combiscope AIST-nt atomic force microscope. The measurement speed is 0.4 Å/s, and the selected area is 1 μm^2. Scanning electron microscopy (SEM) images are recorded on a Gemini 1530 instrument from Carl Zeiss AG. Aiming for good electron conductivity, full-ITO substrate is required for the SEM samples, and Cu tape is used to make connection between the film surface and the metal holder.



BDP-1:C_{60}
1:2 *v/v*
100 °C

BDP-2:C_{60}
1:2 *v/v*
110 °C

BDP-3:C_{60}
1:2 *v/v*
110 °C

Fig. S4. AFM height images, the dimensions are given in nm (top) and SEM images (bottom) of the active layers corresponding to the best performing OSCs

The real absorption in the device is recorded on full devices by measuring the light intensity at the illumination side after reflection at the metal back contact under consideration of vanishing transmission. The reflection characteristics of the evaporated Al contact are taken into account. A halogen and a deuterium lamp are used to cover the full spectral range (Avalight-DH-S-BAL, Avantes). Both illumination and collection of the reflected light is accomplished by a quartz glass fiber, and analyzed by a CAS 140 spectrometer (Instrument System).

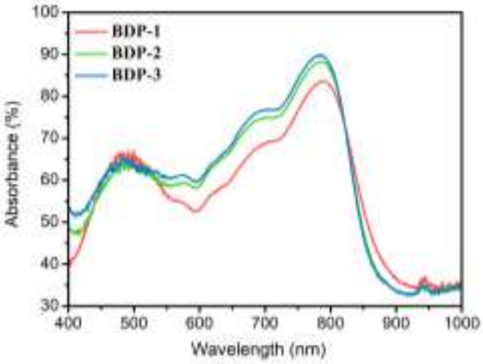


Fig. S5. Absorption spectra of the optimized devices.

7. Nuclear Magnetic Resonance (NMR) Spectroscopy

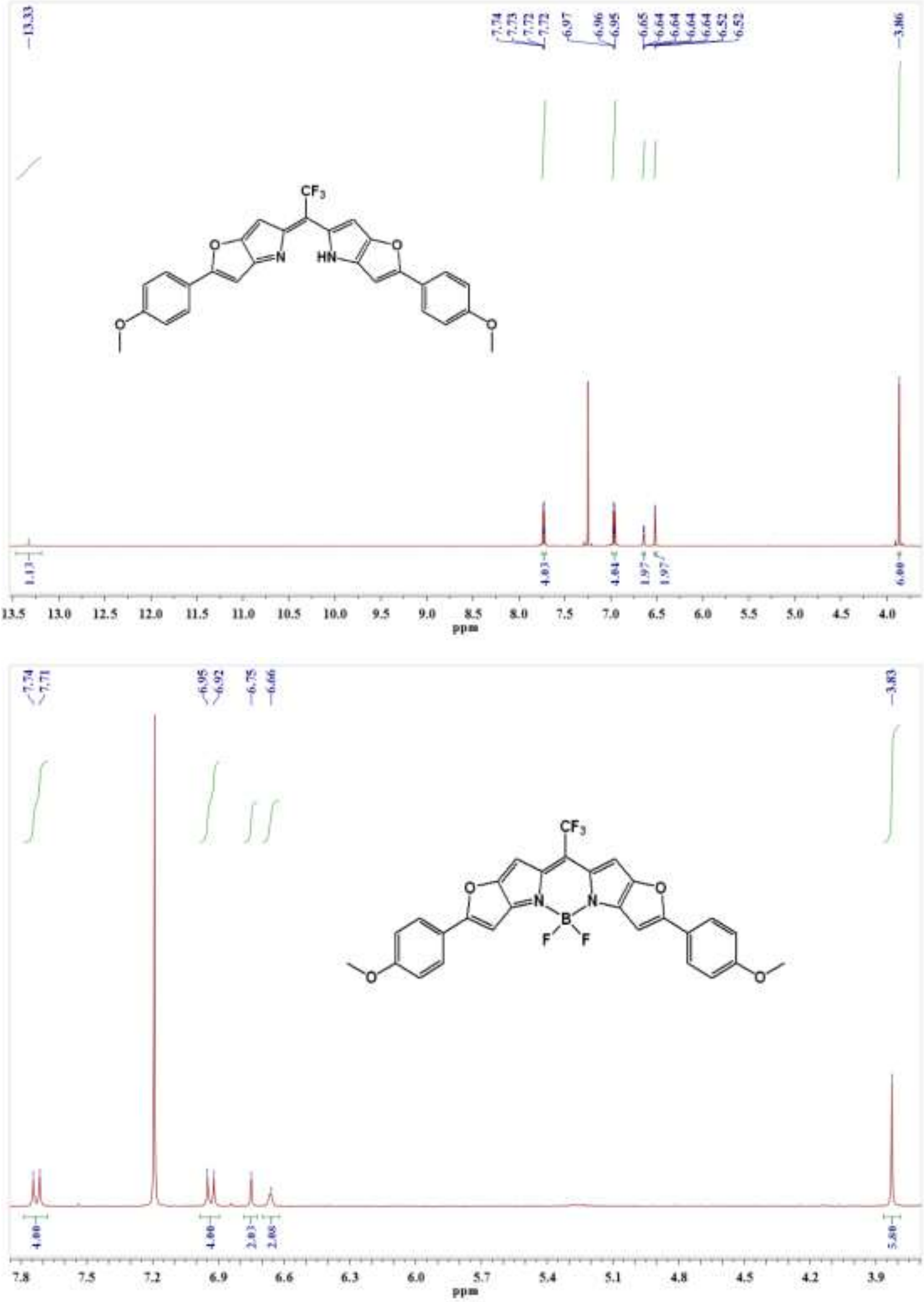
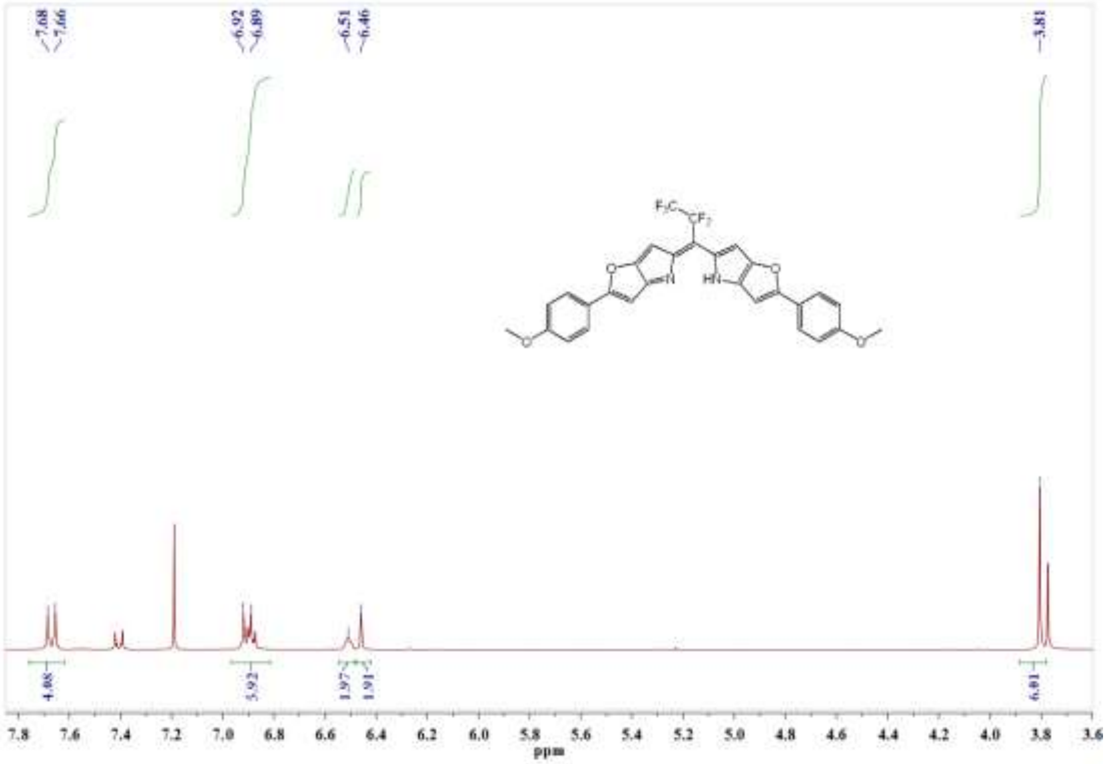


Fig. S6. ^{1}H NMR spectra of **preBDP-1** and **BDP-1**[6]



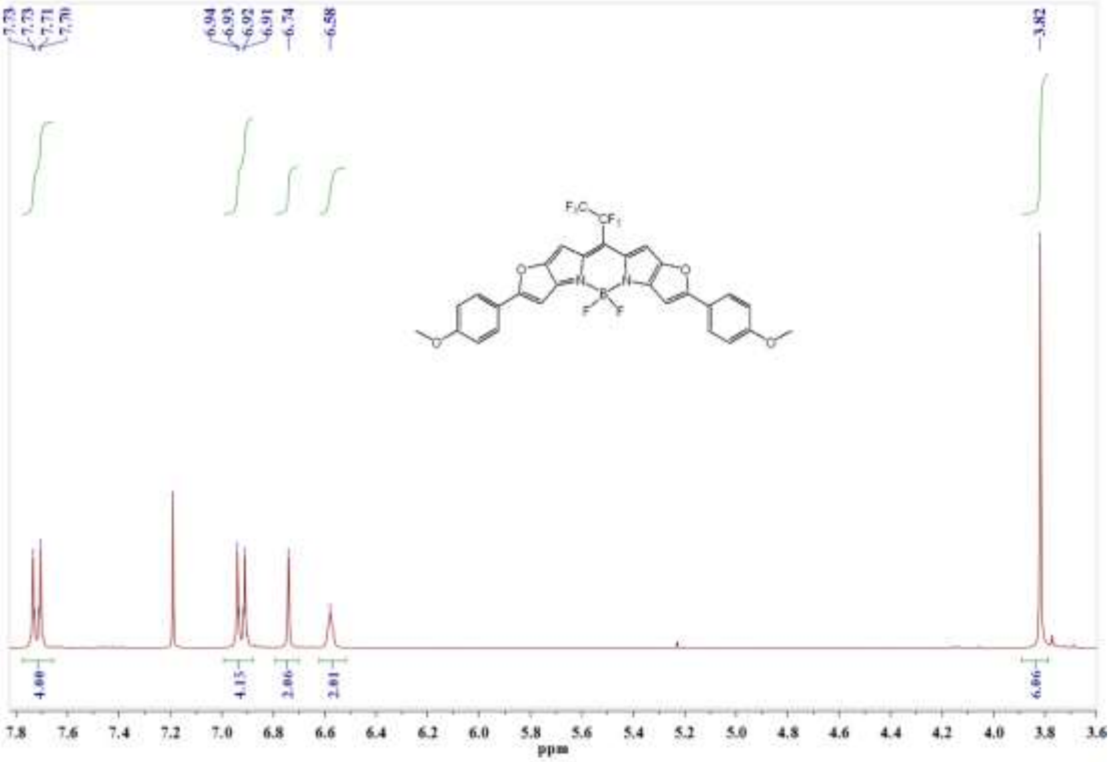


Fig. S7. ^{1}H NMR spectra of **preBDP-2** and **BDP-2**

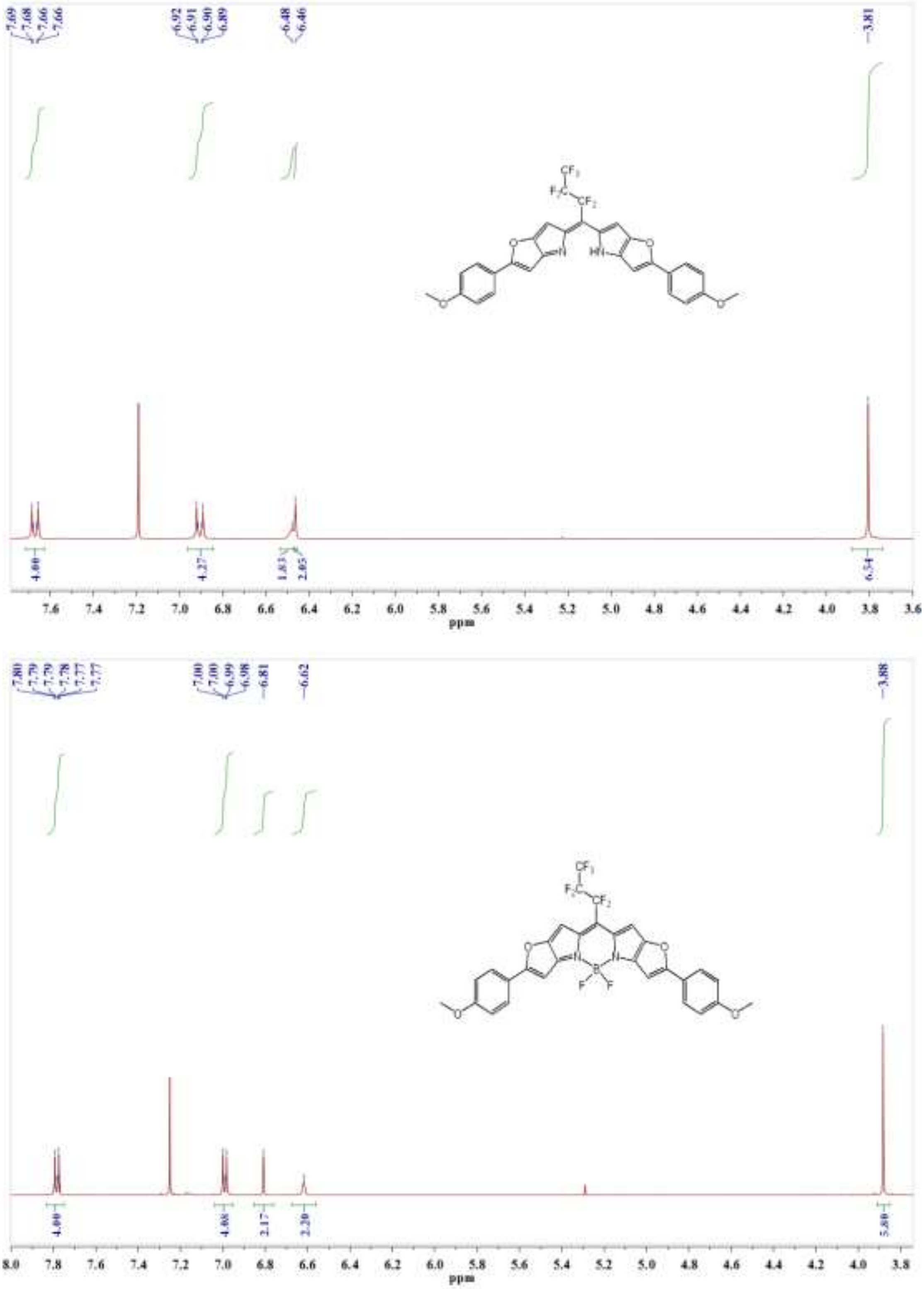


Fig. S8. ^{1}H NMR spectra of **preBDP-3** and **BDP-3**

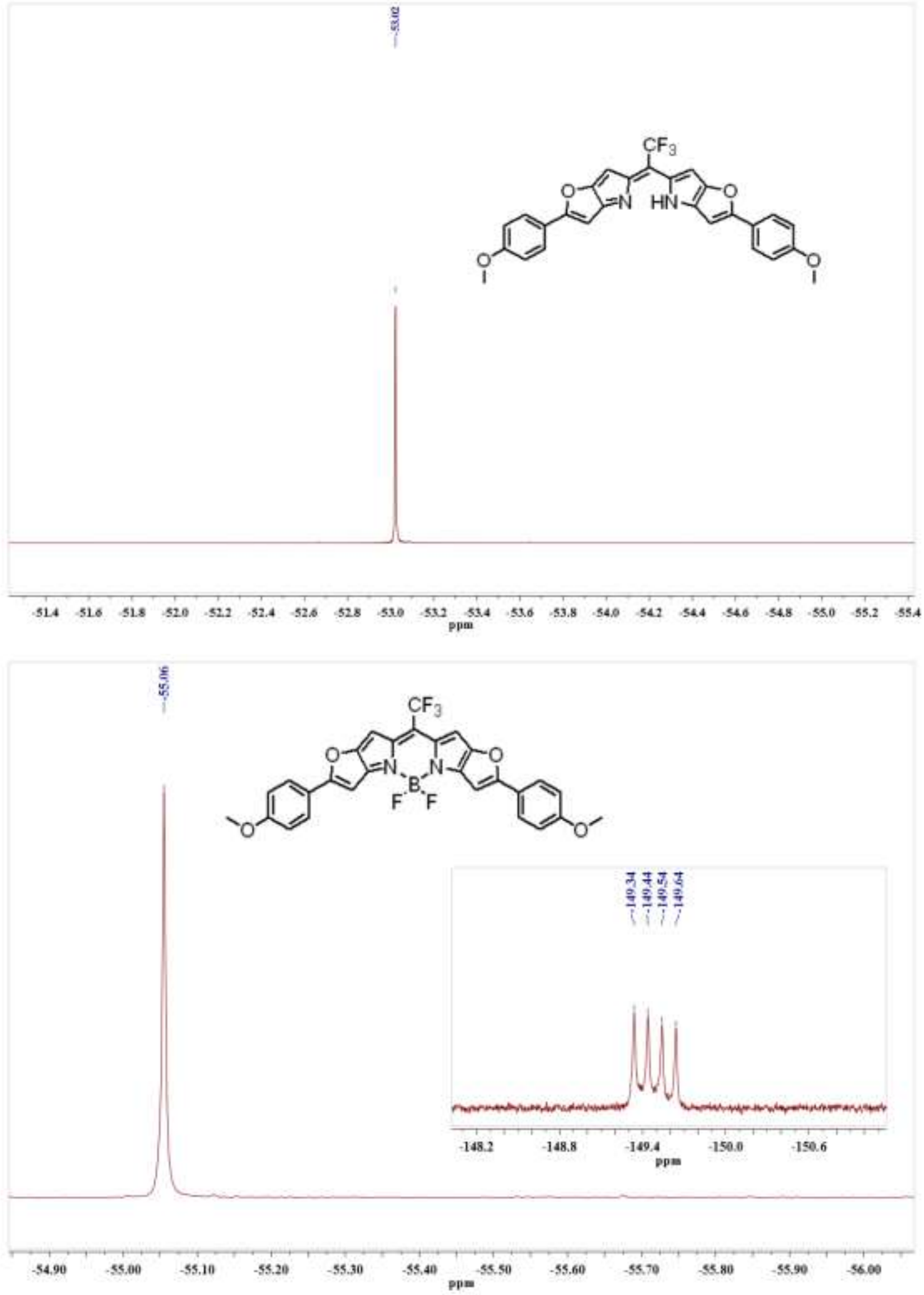


Fig. S9. ^{19}F NMR spectra of **preBDP-1** and **BDP-1**[6]

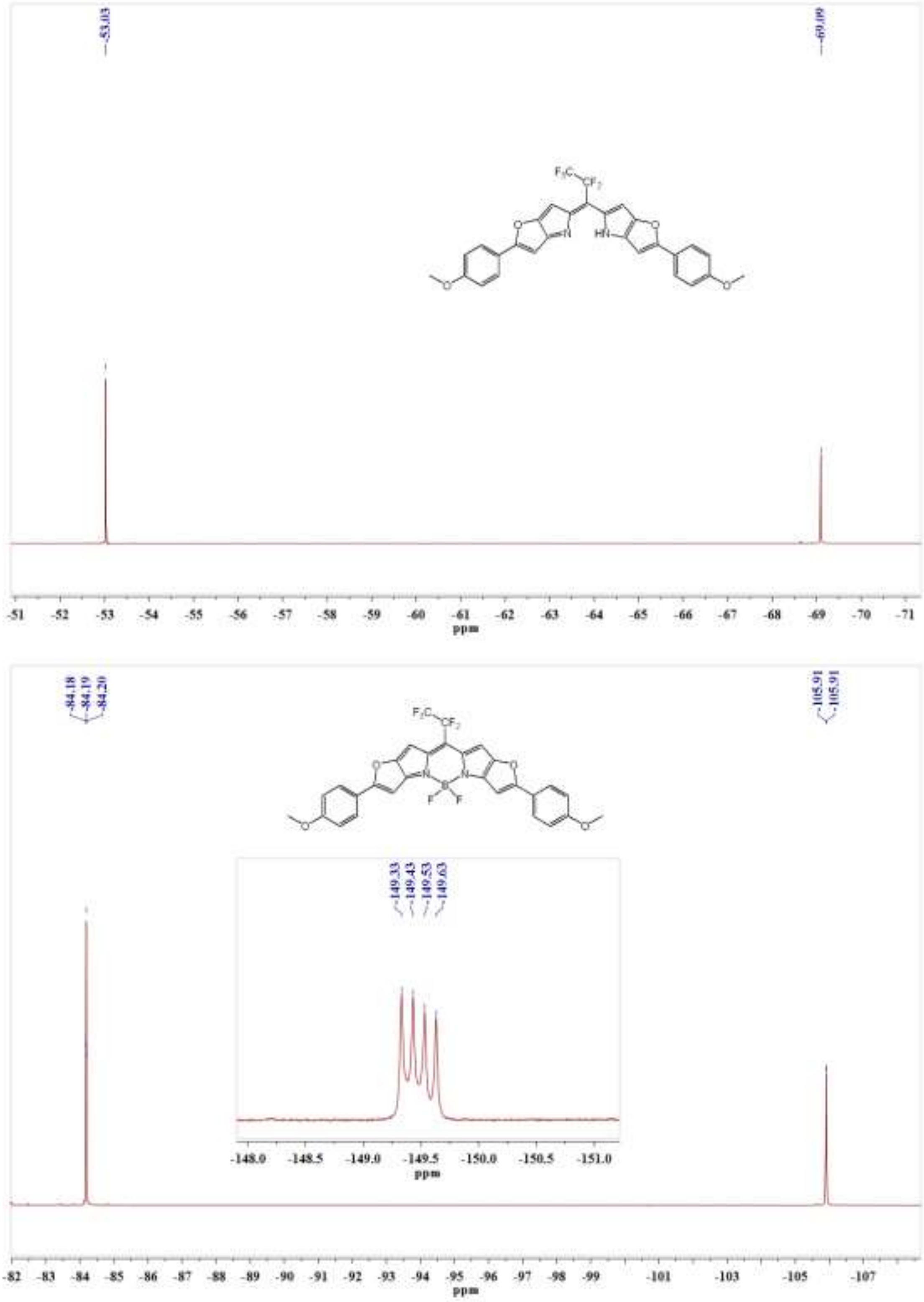


Fig. S10. ^{19}F NMR spectra of **preBDP-2** and **BDP-2**

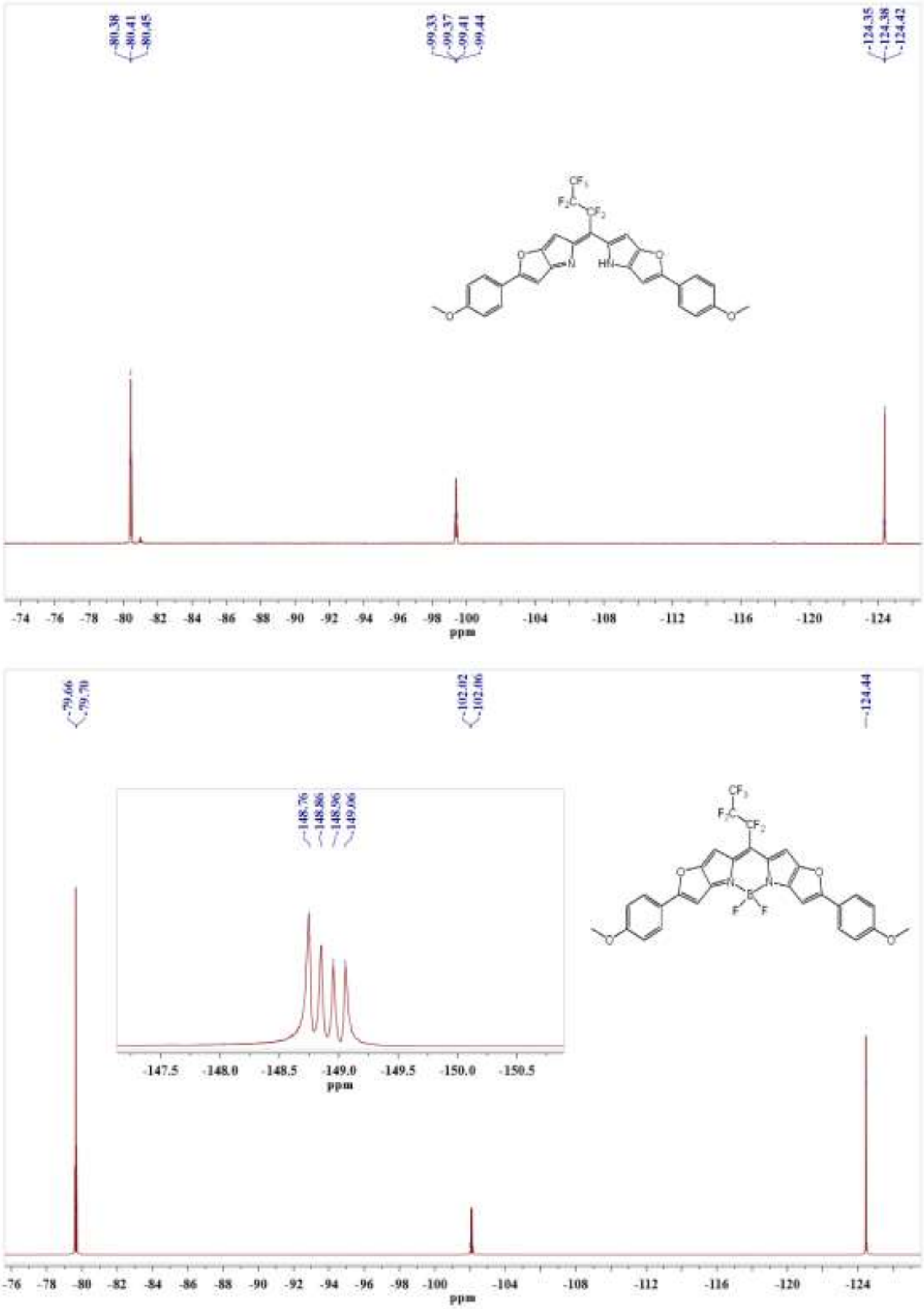


Fig. S11. ^{19}F NMR spectra of **preBDP-3** and **BDP-3**