

***Supporting information for***

**Effects of the nature of donor substituents on the photophysical and electroluminescent properties of derivatives of perfluorobiphenyl: donor-acceptor *versus* donor-acceptor-donor types of AIEE/TADF emitters**

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## ***Instrumentation***

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectra of the solutions in deuterated chloroform ( $\text{CDCl}_3$ ) were obtained using Bruker DRX 400 P (Bruker Avance III) (400 MHz ( $^1\text{H}$ ), 100 MHz ( $^{13}\text{C}$ ), 375 MHz ( $^{19}\text{F}$ )). Chemical shifts ( $\delta$ ) are reported in ppm referenced to tetramethylsilane (TMS). Mass spectra were obtained by the electrospray ionization mass spectrometry (ESI-MS) method on Esquire-LC 00084 mass spectrometer. Elemental analysis data were obtained on a EuroEA Elemental Analyser. The Electrothermal Melt-Temp apparatus (error value of  $\pm 1$  °C) was employed for melting temperatures (mp) measurements of the target compounds. Differential scanning calorimetry (DSC) measurements were done with a PerkinElmer DSC 8500 equipment. The samples were heated at a scan rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 4000 apparatus at a heating rate of 20 °C/min under nitrogen atmosphere.

UV/Vis spectra of  $10^{-4}$  M solutions of the compounds were recorded in quartz cells by Perkin Elmer Lambda 35 spectrometer and UV-VIS-NIR Avantes (AvaSpec-2048XL) spectrophotometer. Photoluminescence (PL) spectra of  $10^{-5}$  M solutions and films of the compounds were recorded at room and low (77K) temperature using Edinburgh Instruments' FLS980 Fluorescence Spectrometer. Thin solid films for recording UV/Vis and PL spectra were prepared by spin-coating technique utilizing SPS-Europe Spin150 Spin processor using 2.5 mg/ml solutions of the compounds in THF on the pre-cleaned quartz substrates. Photoluminescence quantum yields (PLQY) of the solutions and on the solid films were determined using the integrated sphere (Edinburgh Instruments) coupled to the FLS980 spectrometer. PL decay curves and PL intensity dependencies on excitation dose of the doped films at room and low temperatures were measured using a PicoQuant LDH-D-C-375 laser (wavelength 374 nm) equipped to the FLS980 as the excitation source and variable temperature liquid nitrogen cryostat (Optistat DN2).

Electrochemical measurements were done using  $\mu\text{Autolab}$  Type III (EcoChemie, Netherlands) potentiostat, glassy carbon electrode (diam. 2 mm), platinum coil and silver wire as working, auxiliary and reference electrode, respectively and the scan rate of 2.5 mV/s with concentration of compounds  $1.0 \times 10^{-4}$  mol/dm<sup>3</sup>. Potentials are referenced with respect to ferrocene (Fc), which was used as the internal standard. Cyclic voltammetry (CV) experiments were conducted in the dry DMF containing 0.1 M tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as the electrolyte at room temperature under nitrogen atmosphere. Deaeration of the solution was achieved by a nitrogen bubbling for ca. 10 min before measurement. Photoelectron emission spectra for vacuum deposited layers of the studied

compounds were recorded to obtain the solid-state ionization potentials ( $IP_{PE}$ ) of the compounds. Fluorine doped tin oxide (FTO) coated glass slides were used as substrates for the preparation of samples for photoelectron emission spectrometry. The layers of the compounds were fabricated by thermal vacuum evaporation onto the substrates. Photoelectron emission spectra were recorded in air using ASBN-D130-CM deep UV deuterium light source, CM110 1/8m monochromator and 6517B Keithley electrometer.

The synthesized derivatives were studied in electroluminescence devices. Device A was fabricated by vacuum deposition of organic semiconductor layers and metal electrodes onto the pre-cleaned ITO coated glass substrate under vacuum of  $10^{-6}$  Torr. The density-voltage and luminance-voltage characteristics were measured by using a Keithley 6517 Binair without passivation immediately after the preparation of the device. The brightness measurements were carried out by using a calibrated photodiode. The electroluminescence spectra were recorded with Avaspec-2048L spectrometer. Device B was fabricated by vacuum deposition onto pre-cleaned ITO coated glass substrate under vacuum higher than  $2 \times 10^{-6}$  mBar. The deposition rate was up to few Angstroms per second. Density-voltage and luminance-voltage characteristics were recorded simultaneously utilizing Keithley 6517B electrometer, certificated photodiode PH100-Si-HA-D0 together with the PC-Based Power and Energy Monitor 11S-LINK (from STANDA) and Keithley 2400C source meter assuming the lambertian distribution of OLED emission. Electroluminescence (EL) spectra were taken using an Aventes AvaSpec-2048XL spectrometer. Device efficiencies were calculated from the luminance, current density, and EL spectrum. No passivation was done. OLEDs were tested in the ambient atmosphere.

### ***Materials***

The starting materials i.e. phenothiazine, phenoxazine, decafluorobiphenyl potassium hydroxide (KOH) were purchased from Sigma-Aldrich and used as received. 4*H*-Furo[3,2-*b*]indole was obtained according to the previously described procedure[16].

### ***Synthesis***

General procedure for monosubstituted perfluorobiphenyls (**PTZ-PFBP**, **PXZ-PFBP** and **FurInd-PFBP**) synthesis.

To a solution of appropriate amine (phenothiazine, phenoxazine or furo[3,2-b]indole) (1 mmol) in freshly distilled THF (10 mL) was added a hexane solution of *n*-BuLi (0.7 mL, 1.6 M, 1.1 mmol) dropwise at -50°C. After the reaction mixture was stirred for 0.5 h, solution in THF (5 ml) of decafluorobiphenyl (367 mg, 1.1 mmol) was added. The reaction mixture was kept at -40°C for 2 hours and then was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water (25 mL) and extracted with DCM (3×50 mL). The organic layers were collected and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography on silica gel using appropriate eluent system.

**10-(Perfluoro-[1,1'-biphenyl]-4-yl)-10H-phenothiazine PTZ-PFBP.** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/5 eluent system, crystallized from isopropanol and vacuum dried to afford a yellow needle-like crystal (277 mg, 54 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.05 (td, *J* = 7.8, 1.5 Hz, 2H), 6.99 (td, *J* = 8.0, 1.5 Hz, 2H), 6.37 (dd, *J* = 8.0, 1.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.43, 127.44, 127.31, 124.16, 122.51, 115.53. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>) δ -135.92 – -136.22 (m, 2F), -136.76 – -137.02 (m, 2F), -140.96 – -141.25 (m, 2F), -149.22 (tt, *J* = 21.0, 3.0 Hz, 1F), -159.81 – -160.22 (m, 2F). Elemental analysis cal. for C<sub>24</sub>H<sub>8</sub>F<sub>9</sub>NS (%): C, 56.15; H, 1.57; N, 2.72; S, 6.25. Found (%): C, 56.06; H, 1.48; N, 2.83 S, 6.13.

**10-(Perfluoro-[1,1'-biphenyl]-4-yl)-10H-phenoxazine PXZ-PFBP.** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/3 eluent system, crystallized from ethyl acetate with hexane and vacuum dried to afford light-yellow crystals (313 mg, 63 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.87 – 6.74 (m, 6H), 6.12 (d, *J* = 7.6 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.07, 130.94, 123.68, 123.30, 116.40, 112.79. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>) δ -135.78 – -135.99 (m, 2F), -136.80 – -137.03 (m, 2F), -141.24 (dd, *J* = 22.2, 11.2 Hz, 2F), -149.20 (tt, *J* = 21.0, 3.0 Hz, 1F), -159.77 – -160.20 (m, 2F). MS (ES+, 1.04 eV), *m/z*: cal. for C<sub>24</sub>H<sub>8</sub>F<sub>9</sub>NO 497.31 [M<sup>+</sup>], found 497.79.

Elemental analysis cal. for C<sub>24</sub>H<sub>8</sub>F<sub>9</sub>NO (%): C, 57.96; H, 1.62; N, 2.82. Found (%): C, 57.82; H, 1.74; N, 2.70.

**4-(Perfluoro-[1,1'-biphenyl]-4-yl)-4H-furo[3,2-b]indole) FurInd-PFBP.** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/5 eluent system, crystallized from isopropanol with DMF and vacuum dried to afford a white solid (335 mg, 71 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 – 7.82 (m, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 7.36 – 7.29 (m, 3H), 6.63 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 146.23, 143.07, 139.51, 131.76, 122.85, 121.90, 116.82, 116.10, 111.82, 99.79. <sup>19</sup>F NMR (375 MHz, CDCl<sub>3</sub>) δ -136.70 – -137.21 (m, 4F), -143.04 – -143.44 (m, 2F), -149.53 (dd, *J* = 30.0, 11.9 Hz, 1F), -159.73 – -160.36 (m, 2F). Elemental analysis cal. for C<sub>22</sub>H<sub>6</sub>F<sub>9</sub>NO (%): C, 56.07; H, 1.28; N, 2.97. Found (%): C, 56.21; H, 1.16; N, 3.08.

General procedure for disubstituted perfluorobiphenyls (**2PTZ-PFBP**, **2PXZ-PFBP** and **2FurInd-PFBP**) synthesis.

To a solution of appropriate amine (phenothiazine, phenoxazine, furo[3,2-b]indole) (2 mmol) in DMSO (10 mL) was added KOH (123 mg, 2.2 mmol) previously well grounded in a mortar. Solution was stirred 0.5 hour. During this time almost all potassium hydroxide was dissolved providing colored solutions. Obtained liquid was added dropwise via syringe to well stirred solution of decafluorobiphenyl (334 mg, 1 mmol) in DMSO (5 ml). The resultant mixture was stirred at r.t. overnight. The reaction mixture was quenched with water (50 mL) sediment was filtrated, washed well with distilled water and then dried. The crude product was purified by flash column chromatography on silica gel using appropriate eluent system.

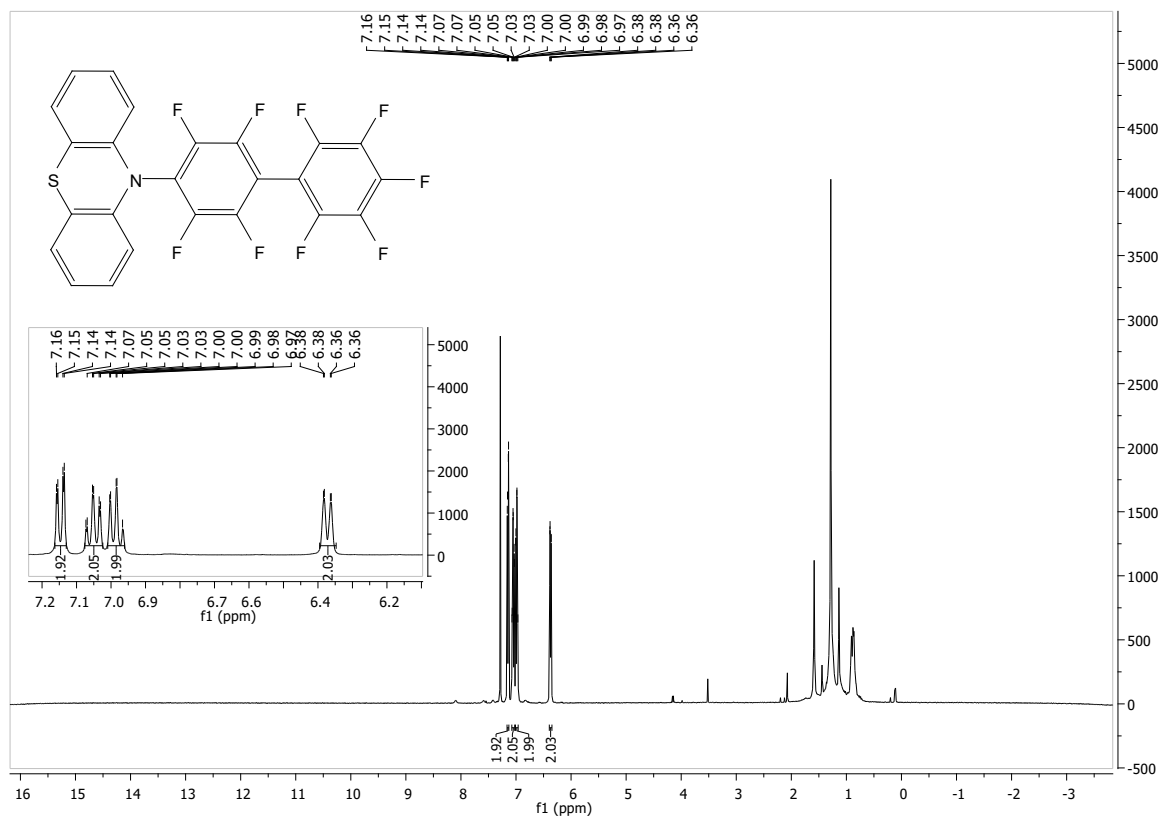
**10,10'-(Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(10H-phenothiazine) 2PTZ-PFBP.** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/5 eluent system, crystallized from isopropanol with DMF and vacuum dried to afford a yellow microcrystals (360 mg, 52 % yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.16 (dd, *J* = 7.5, 1.5 Hz, 4H), 7.07 (td, *J* = 7.8, 1.6 Hz, 4H),

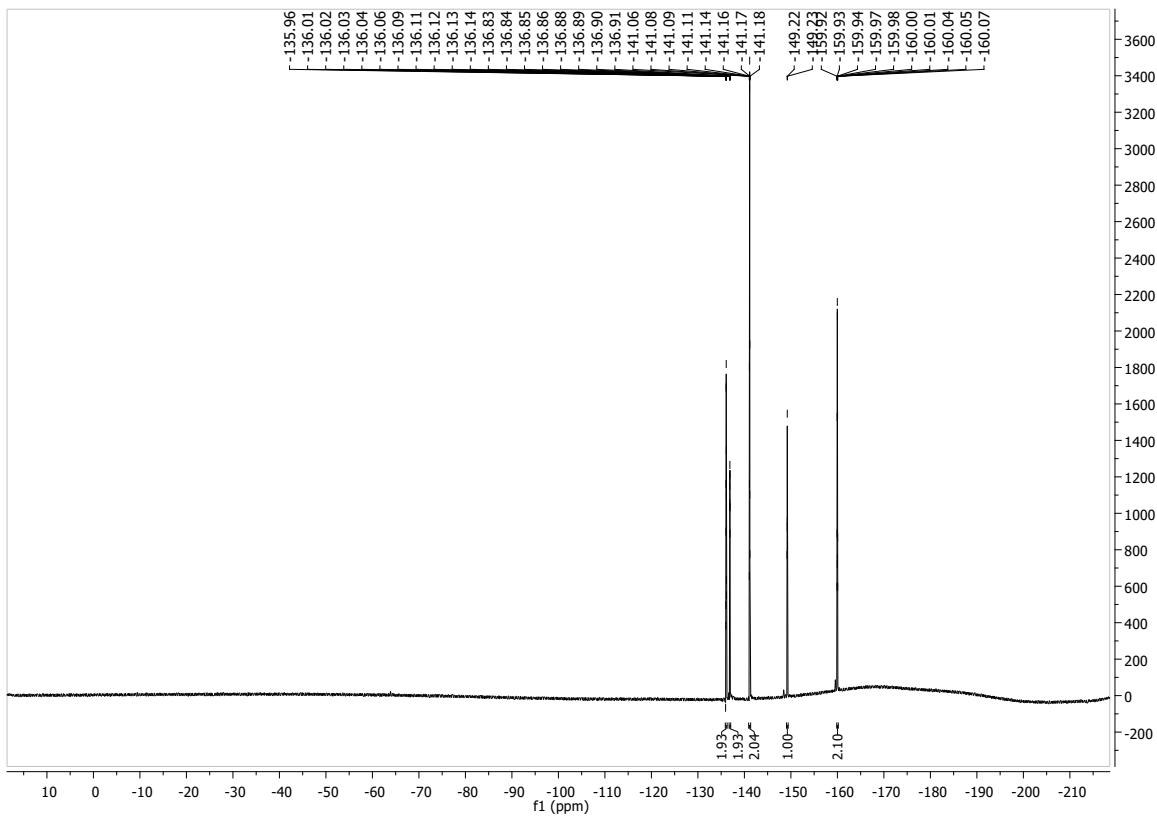
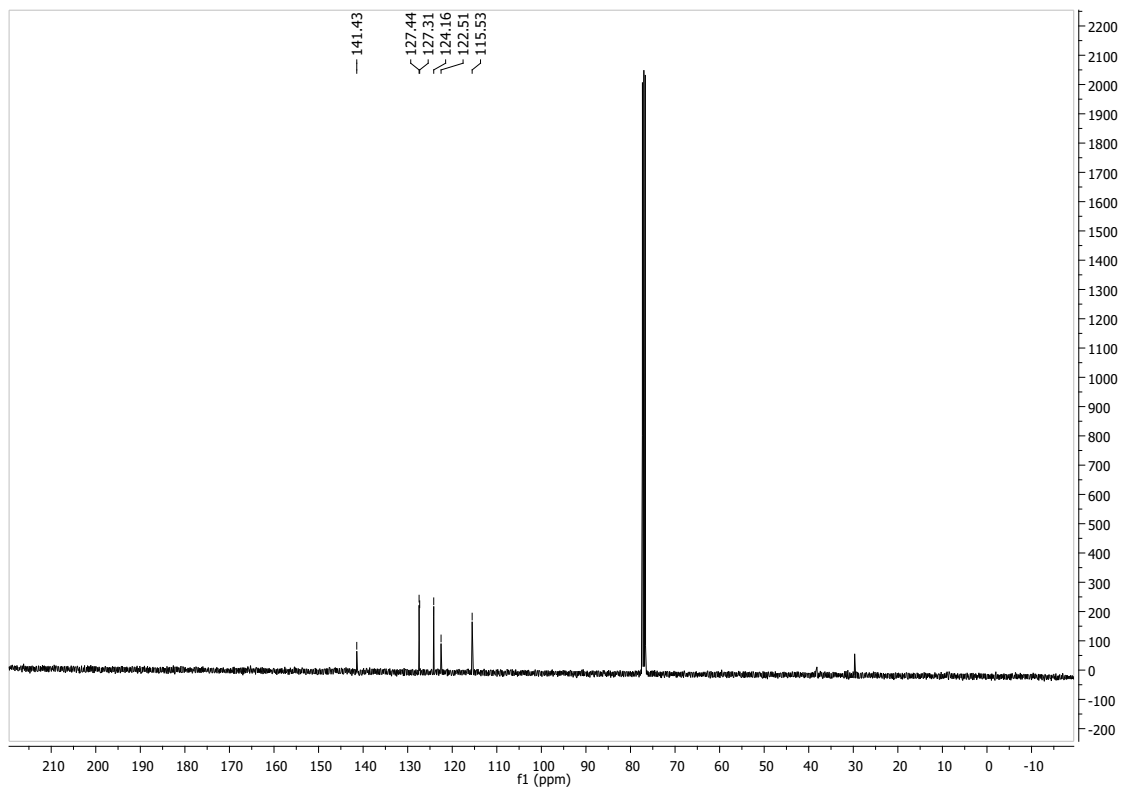
7.00 (td,  $J = 7.5, 1.0$  Hz, 4H), 6.41 (d,  $J = 7.2$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.45, 127.49, 127.37, 124.22, 122.55, 115.57.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ )  $\delta$  -135.50 – -135.77 (m, 4F), -140.93 (dd,  $J = 23.4, 11.1$  Hz, 4F). MS (ES+, 1.04 eV),  $m/z$ : cal. for  $\text{C}_{36}\text{H}_{16}\text{F}_8\text{N}_2\text{S}_2$  692.62 [ $\text{M}^+$ ], found 692.38. Elemental analysis cal. for  $\text{C}_{36}\text{H}_{16}\text{F}_8\text{N}_2\text{S}_2$  (%): C, 62.43; H, 2.33; N, 4.04; S, 9.26. Found (%): C, 62.31; H, 2.46; N, 3.95; S, 9.13.

***10,10'-(Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(10H-phenoxazine) 2PXZ-PFBP.*** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/3 eluent system, crystallized from isopropanol with DMF and vacuum dried to afford a bright yellow crystalline mass (495 mg, 75 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 – 6.77 (m, 12H), 6.15 (d,  $J = 7.5$  Hz, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  144.10, 130.94, 123.71, 123.35, 116.44, 112.82.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ )  $\delta$  -135.34 – -135.66 (m, 4F), -140.95 (dd,  $J = 23.7, 11.0$  Hz, 4F). MS (ES+, 1.04 eV),  $m/z$ : cal. for  $\text{C}_{36}\text{H}_{16}\text{F}_8\text{N}_2\text{O}_2$  660.51 [ $\text{M}^+$ ], found 660.73. Elemental analysis cal. for  $\text{C}_{36}\text{H}_{16}\text{F}_8\text{N}_2\text{O}_2$  (%): C, 65.46; H, 2.44; N, 4.24. Found (%): C, 65.57; H, 2.36; N, 4.11.

***4,4'-(Perfluoro-[1,1'-biphenyl]-4,4'-diyl)bis(4H-furo[3,2-b]indole) 2FurInd-PFBP.*** The crude product was purified by flash column chromatography on silica gel using DCM/HEX=1/5 eluent system, crystallized from isopropanol with hexane and vacuum dried to afford white powder (420 mg, 69 % yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.78 (m, 2H), 7.63 (d,  $J = 2.0$  Hz, 2H), 7.37 – 7.29 (m, 6H), 6.64 (s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.22, 143.14, 139.58, 131.81, 122.87, 121.92, 116.83, 116.15, 111.86, 99.82.  $^{19}\text{F}$  NMR (375 MHz,  $\text{CDCl}_3$ )  $\delta$  -136.40 – -136.89 (m, 4F), -143.17 (d,  $J = 11.8$  Hz, 4F). Elemental analysis cal. for  $\text{C}_{32}\text{H}_{12}\text{F}_8\text{N}_2\text{O}_2$  (%): C, 63.17; H, 1.99; N, 4.60. Found (%): C, 63.08; H, 1.83; N, 4.48.

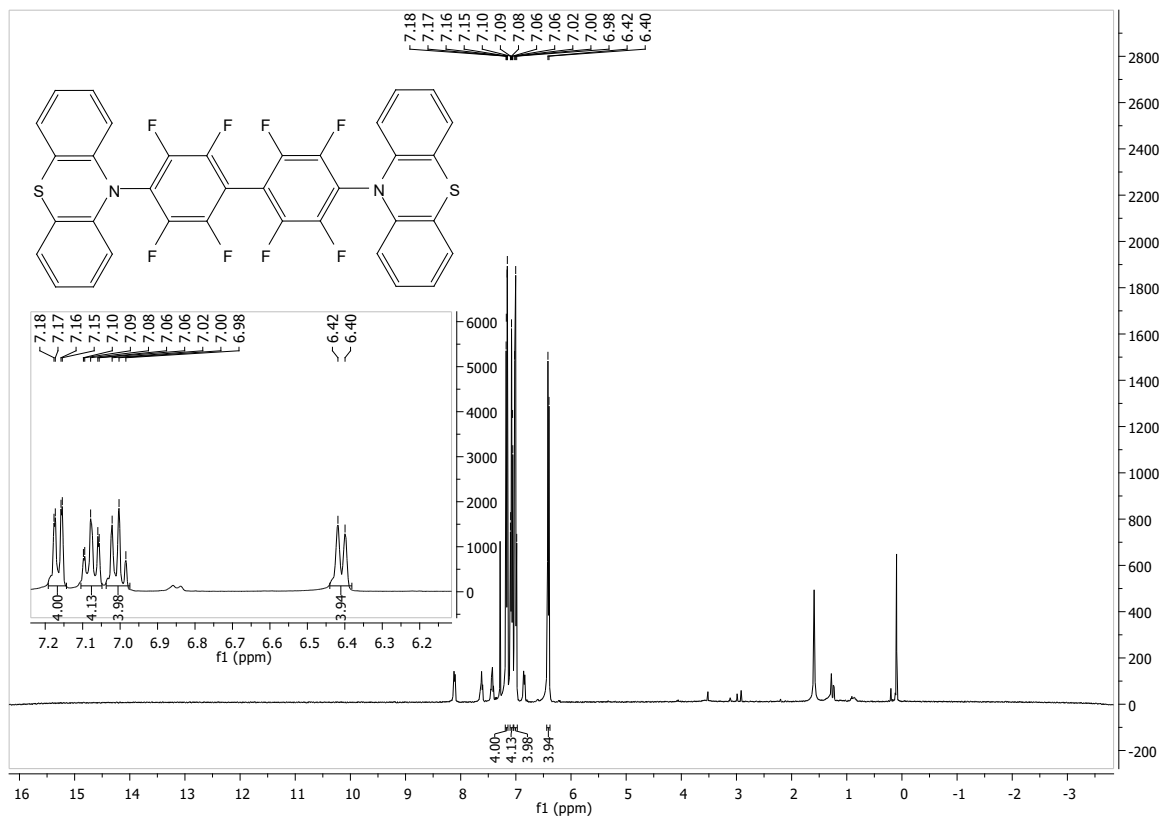
# <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F spectra of PTZ-PFBP

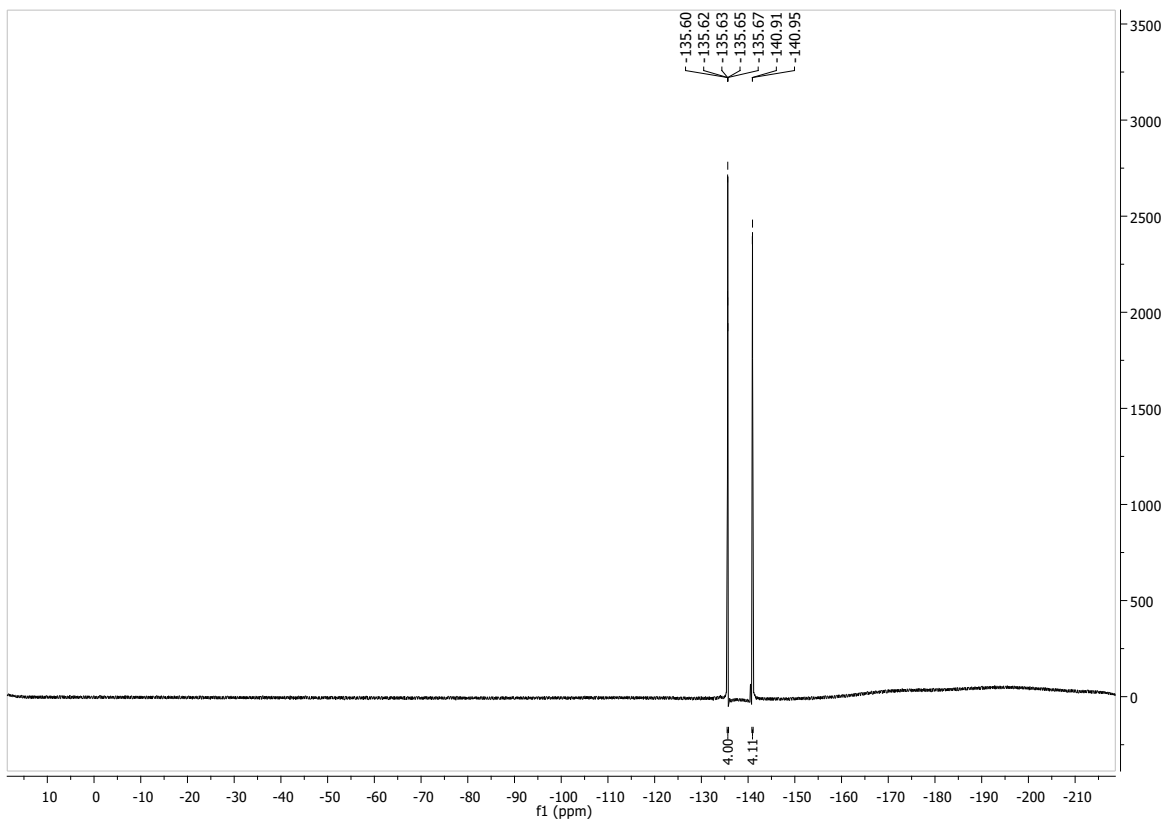
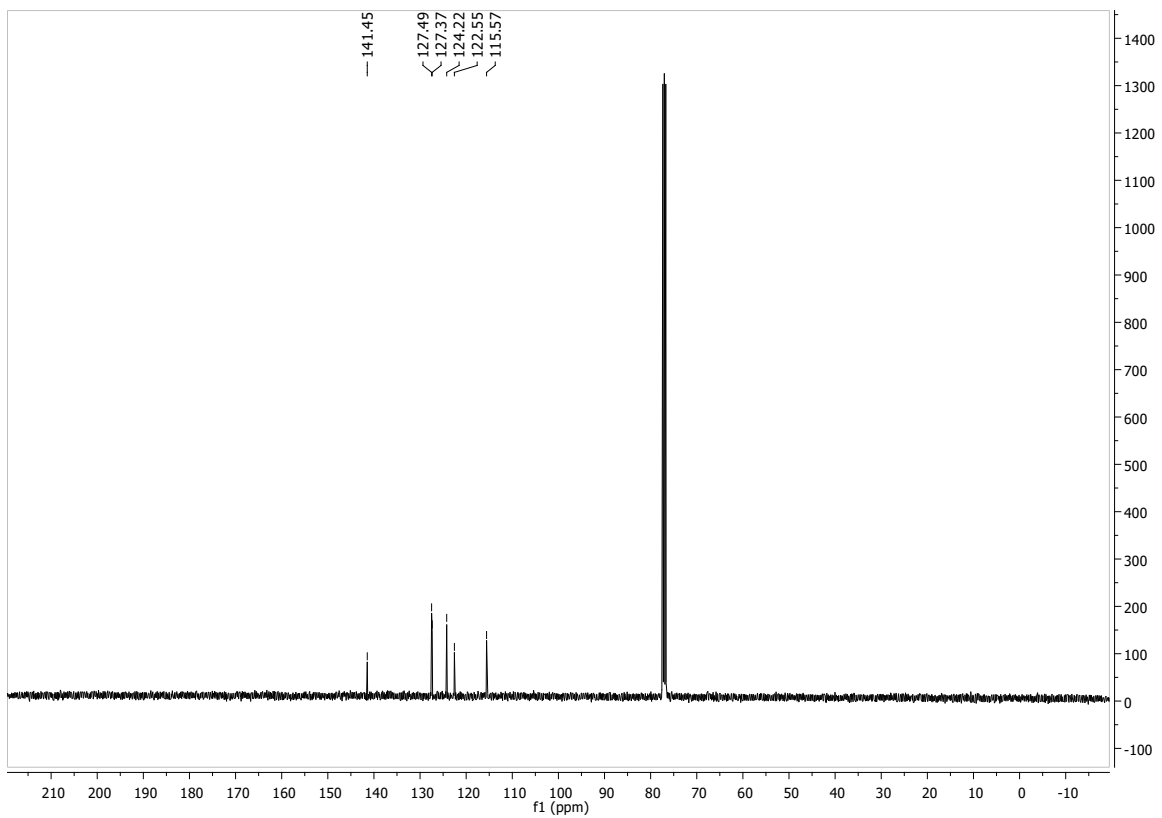




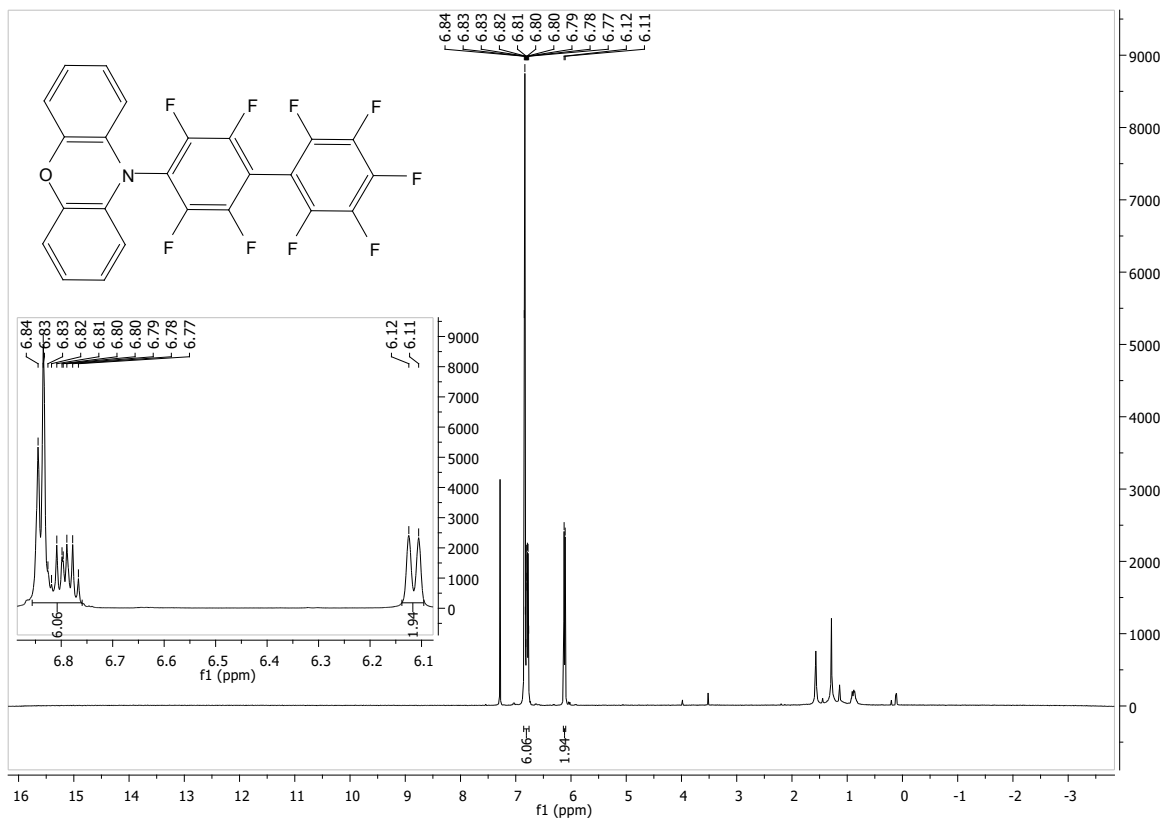


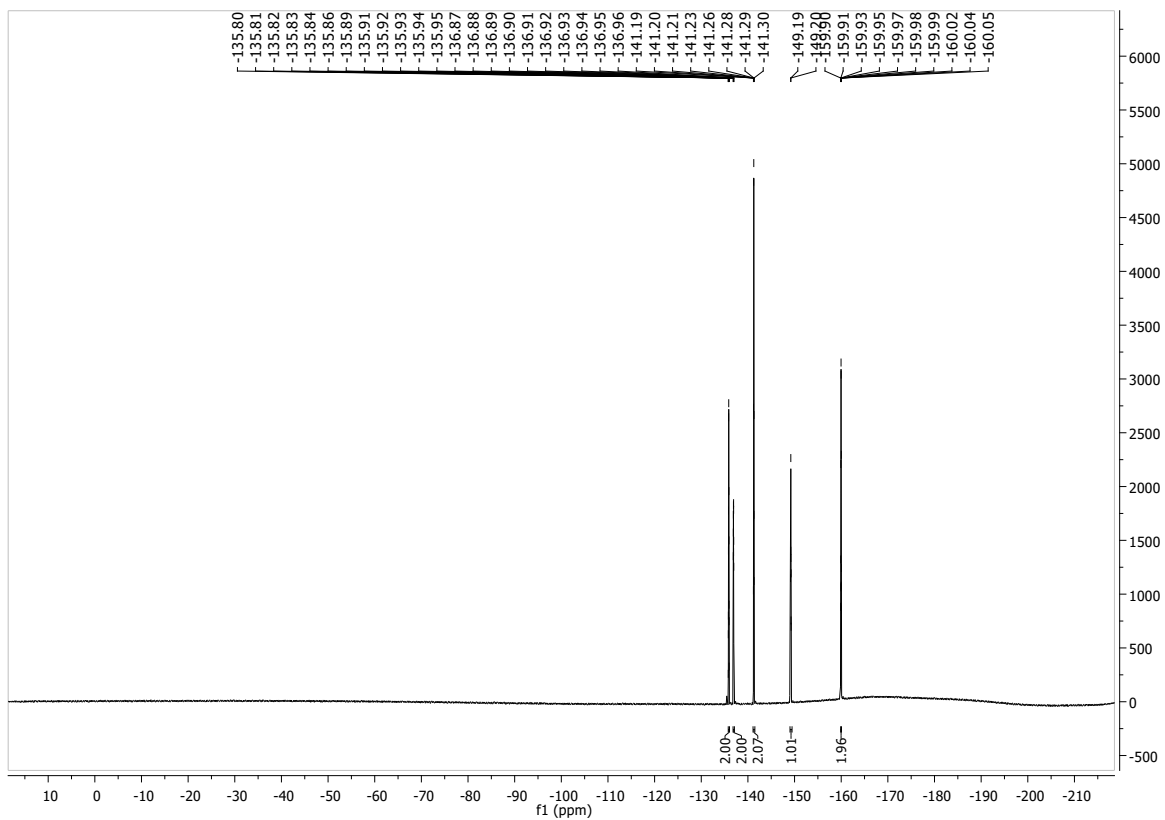
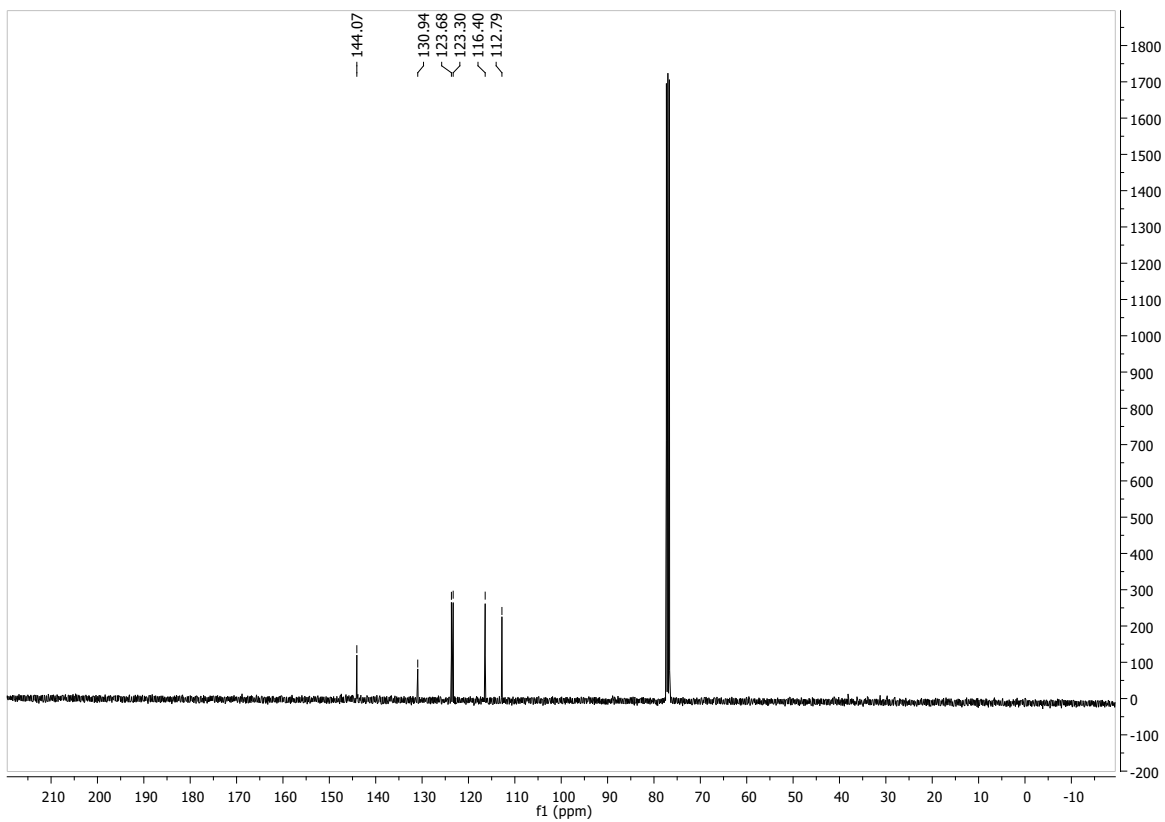
# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra of 2PTZ-PFBP



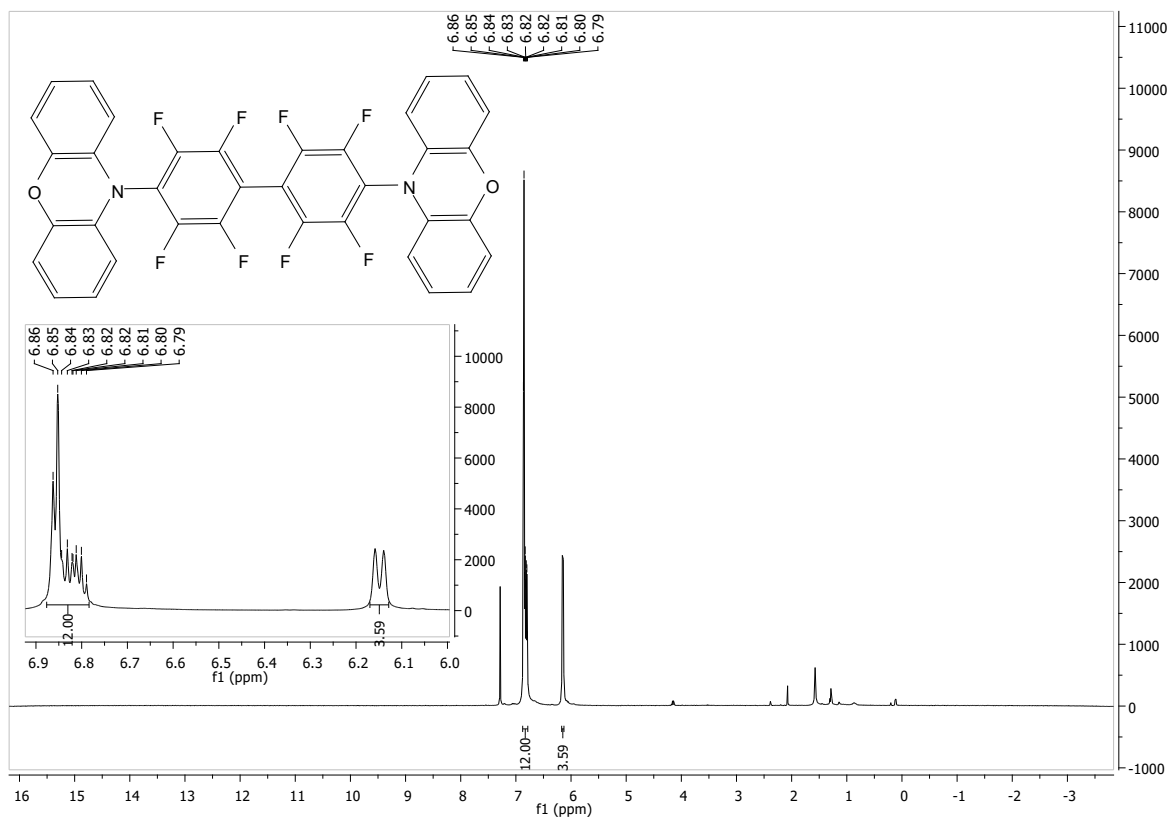


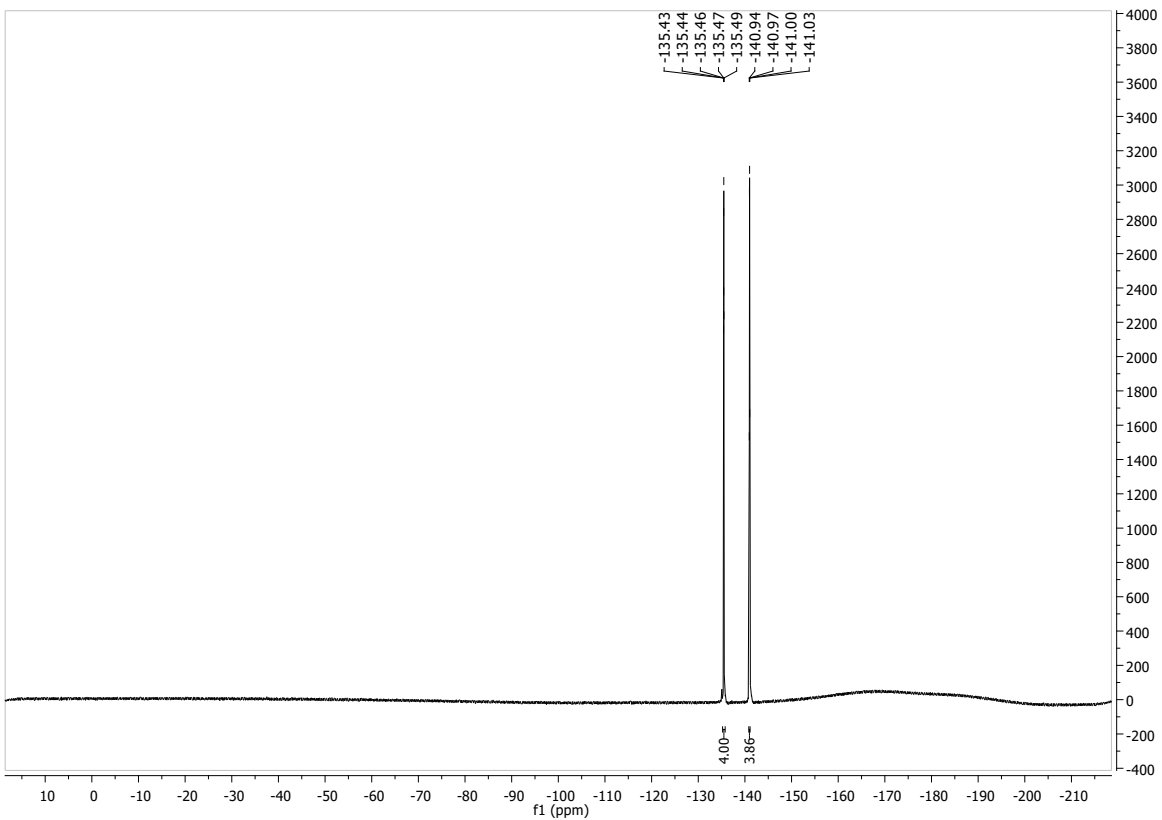
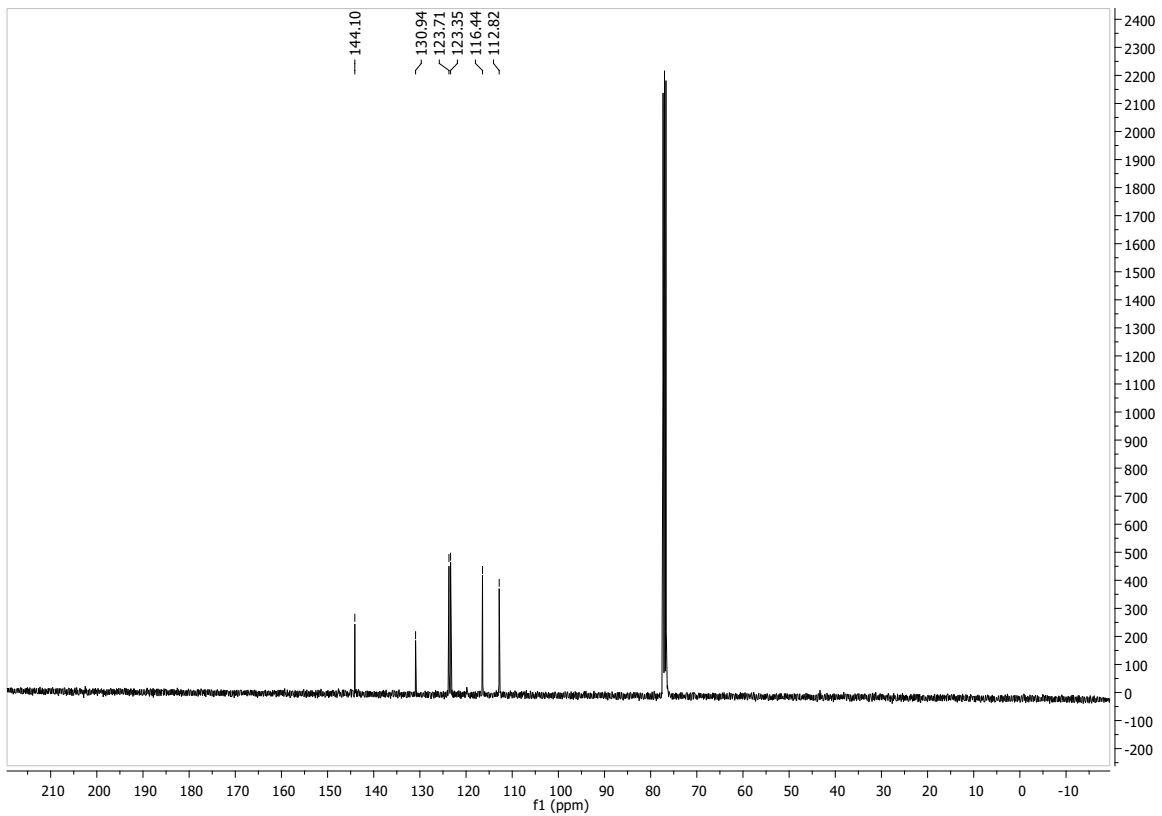
# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra of PXZ-PFBP



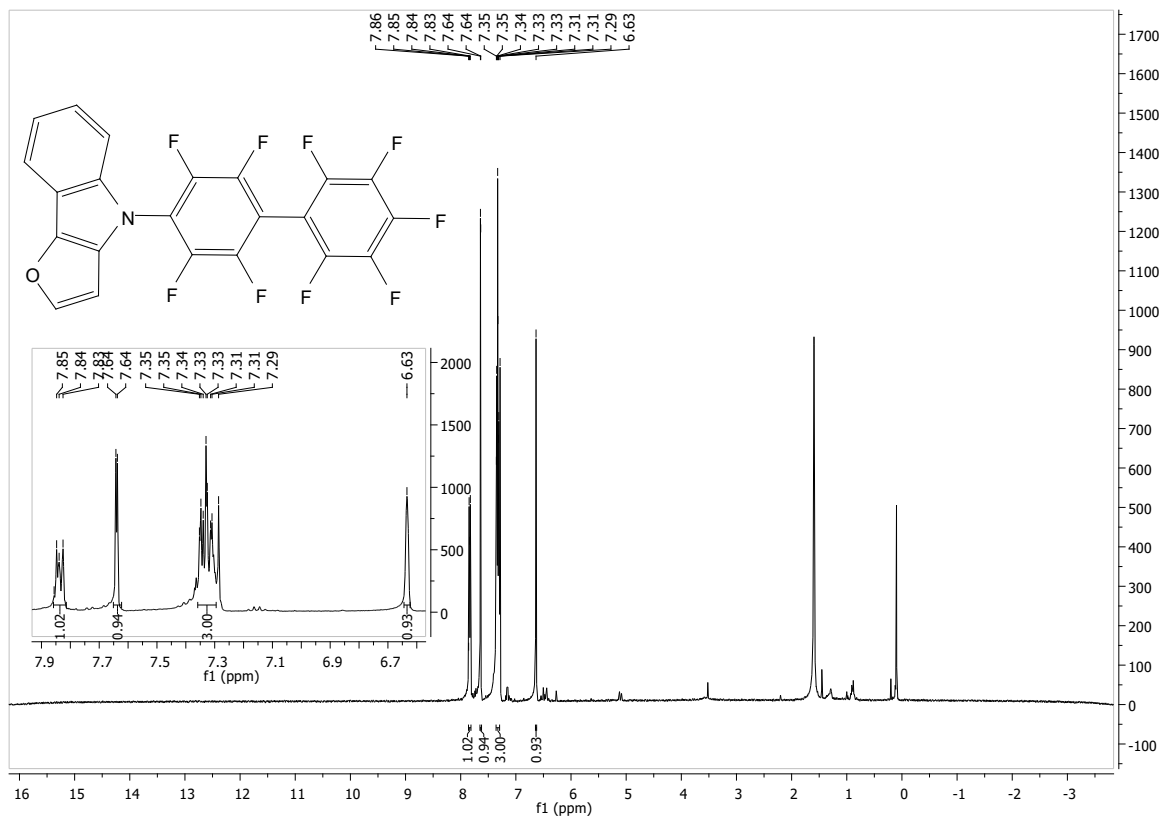


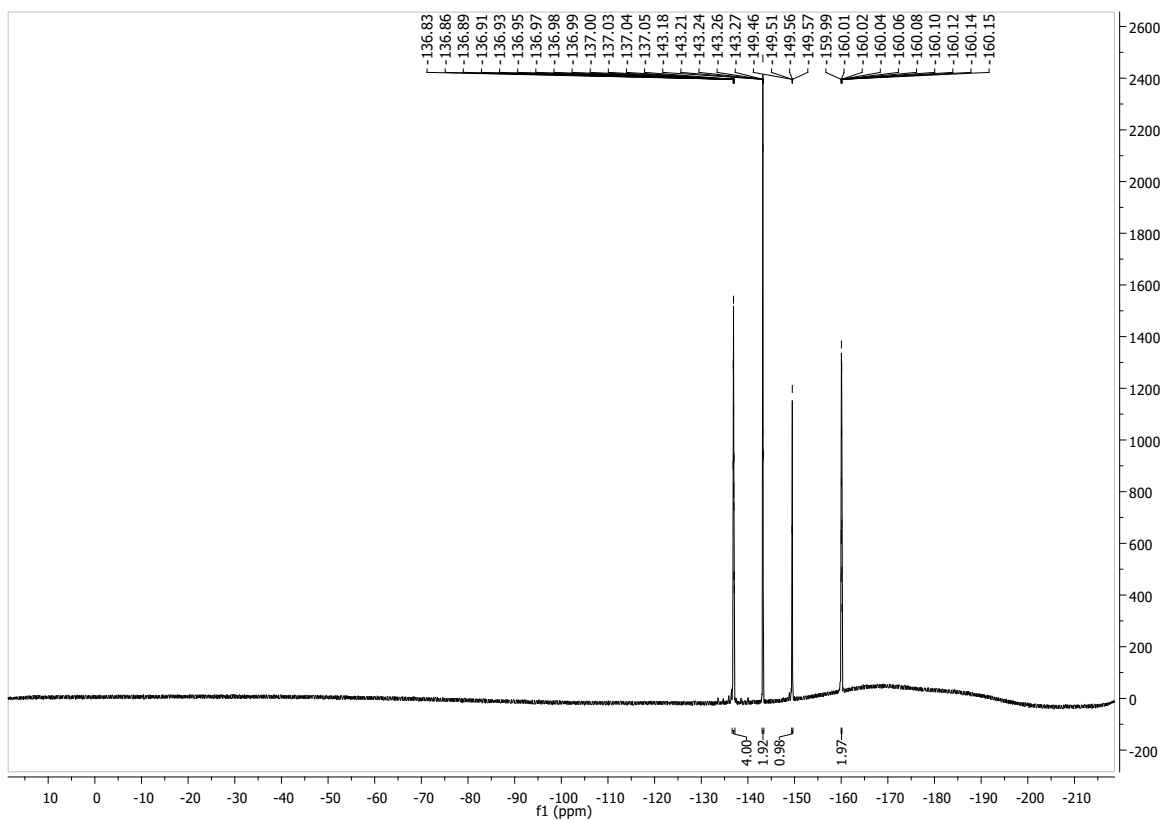
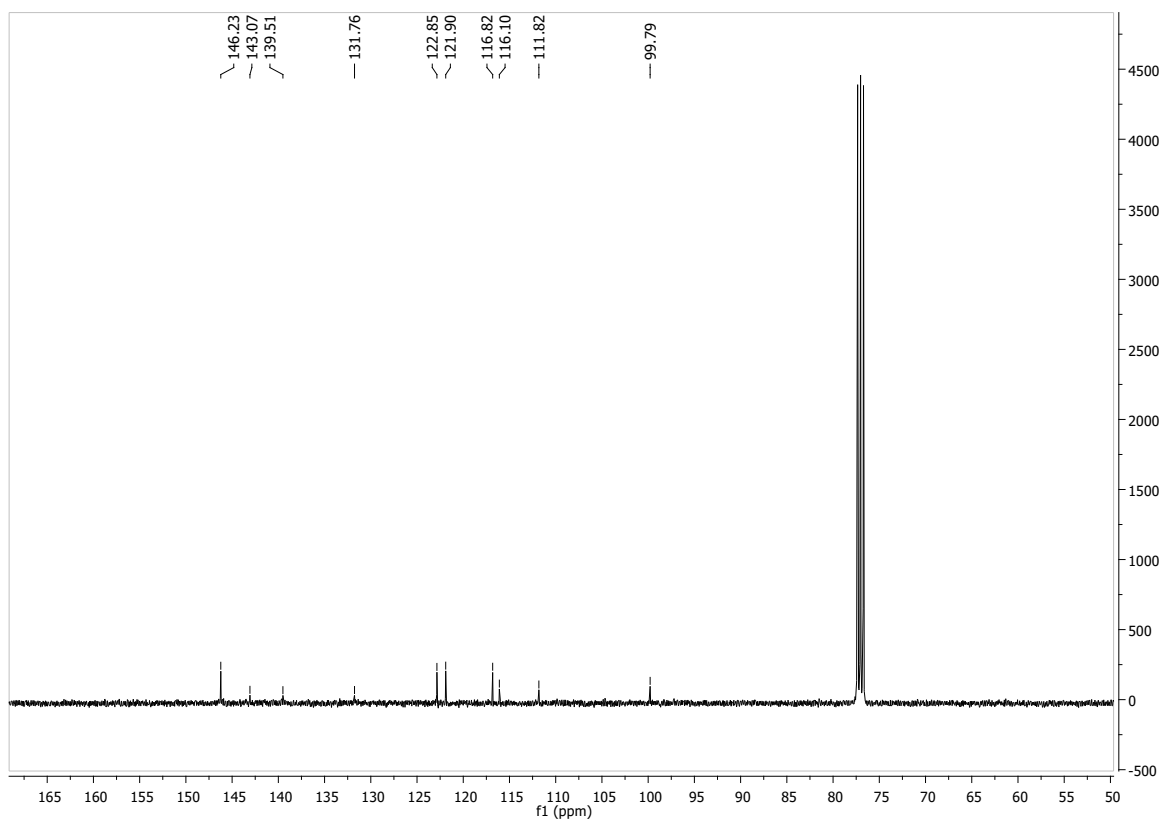
# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra of 2PXZ-PFBP





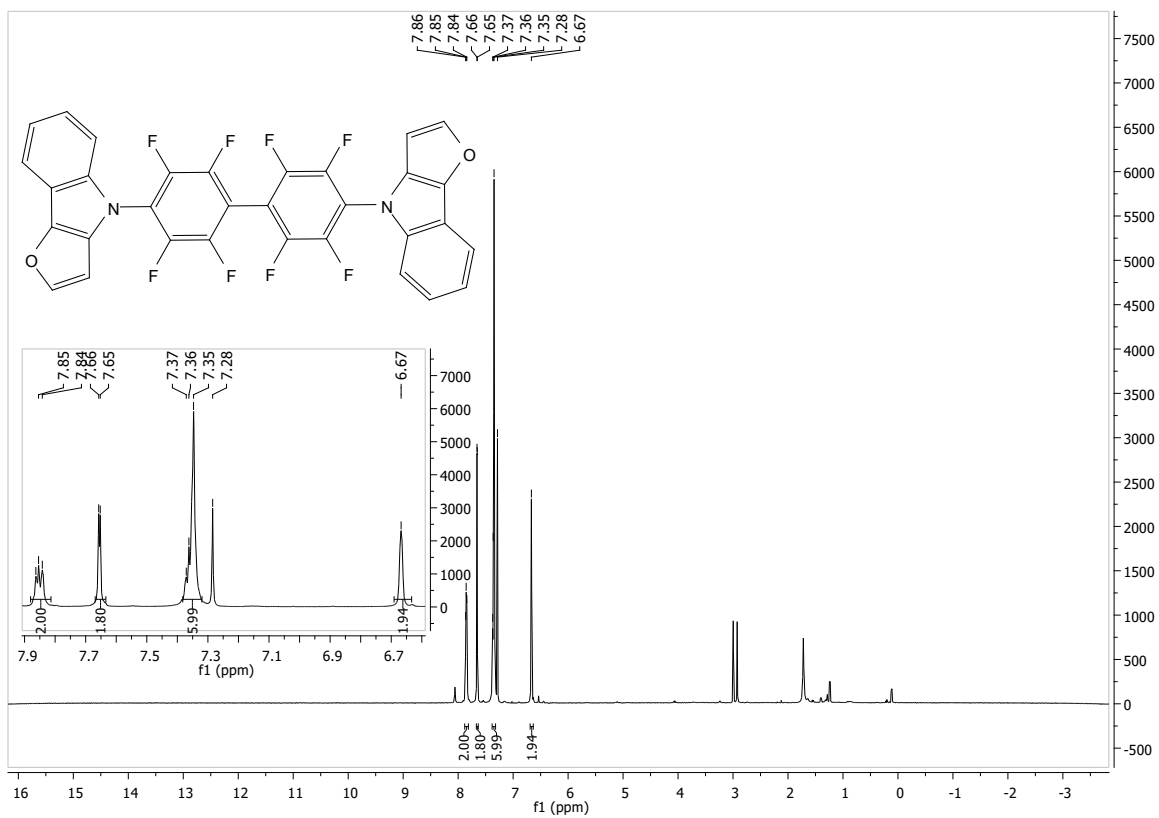
# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra of FurInd-PFBP

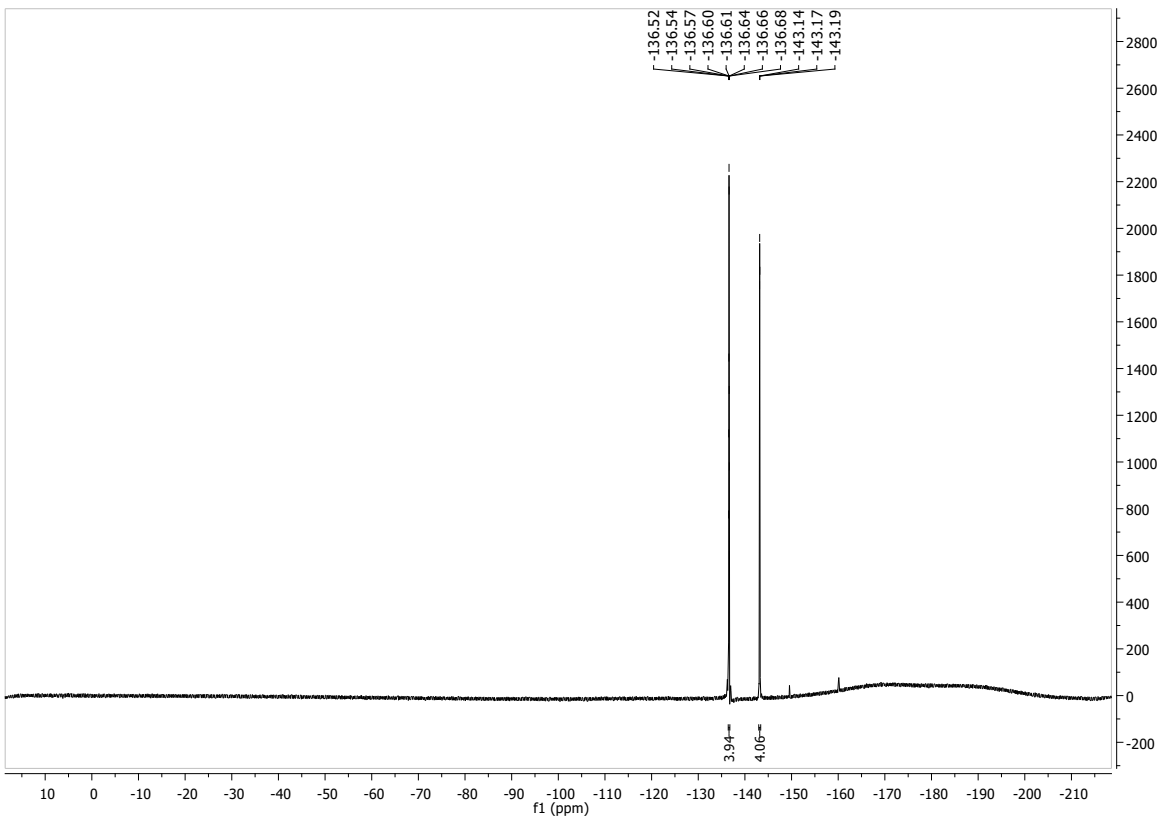
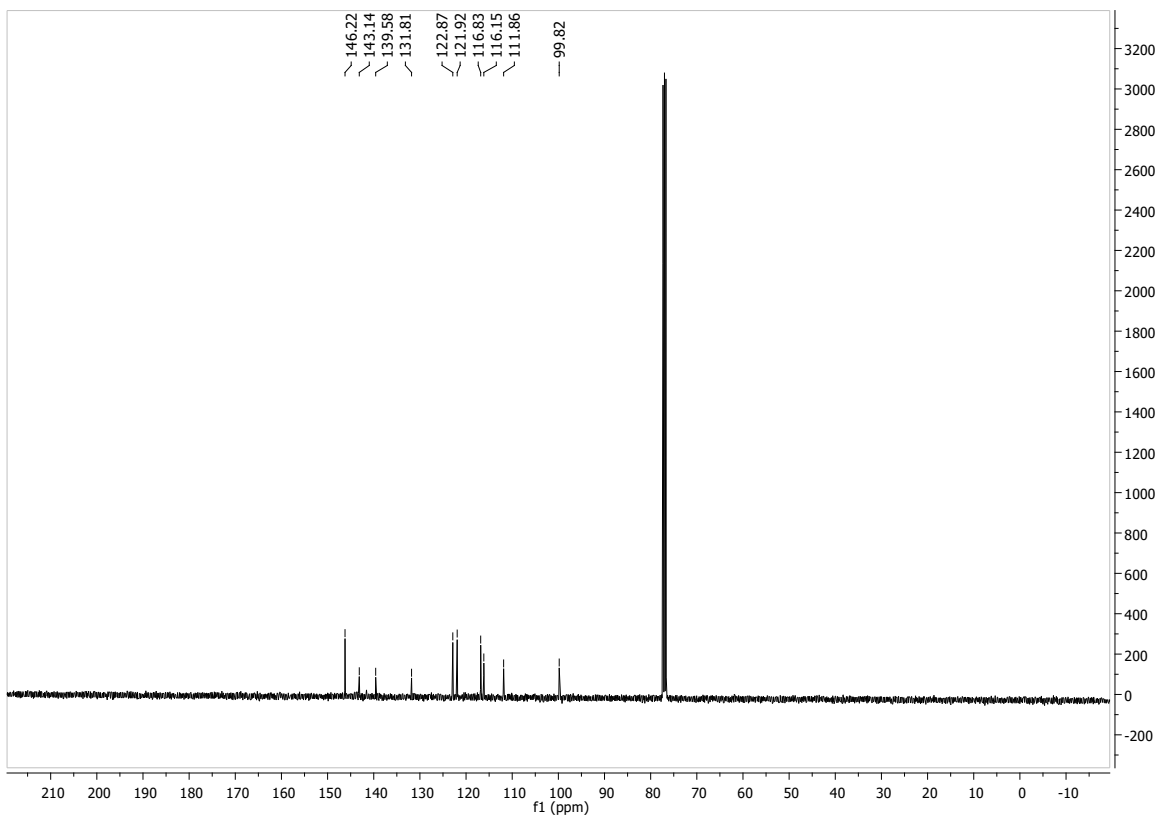




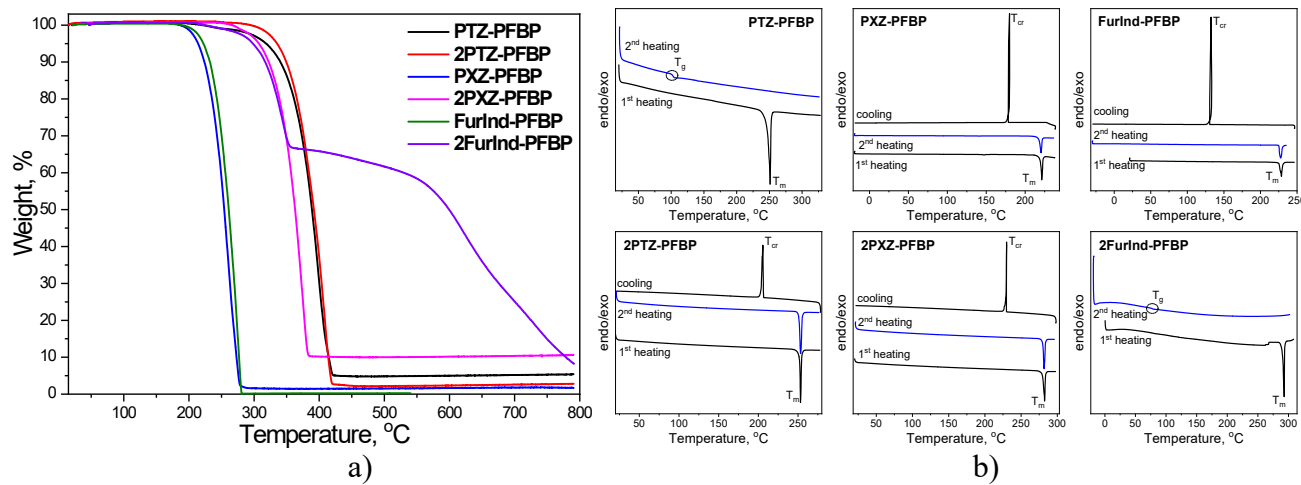


# $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ spectra of 2FurInd-PFBP



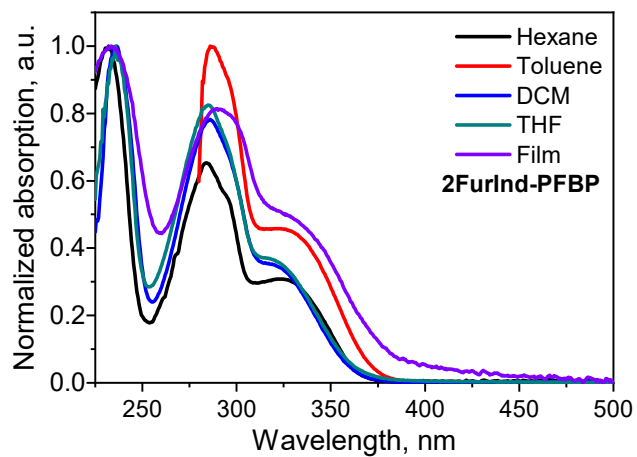
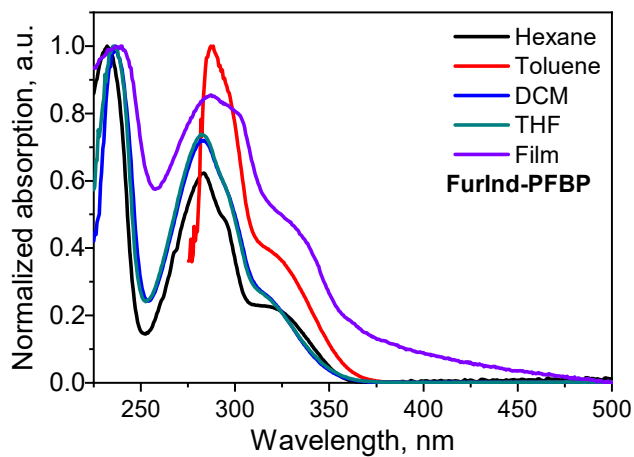
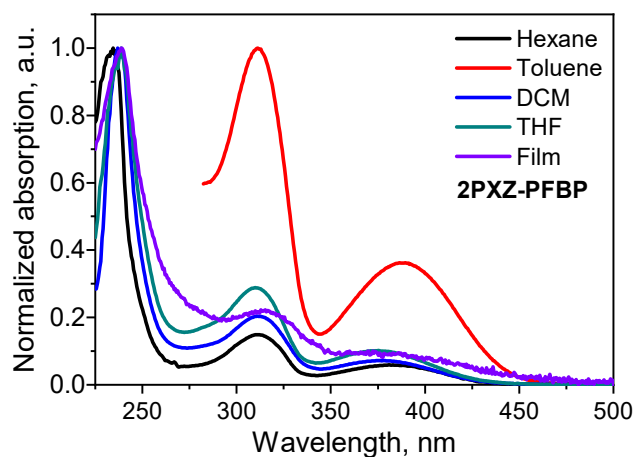
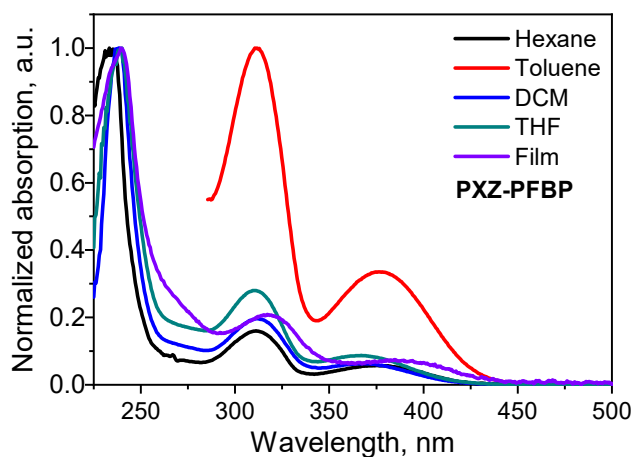
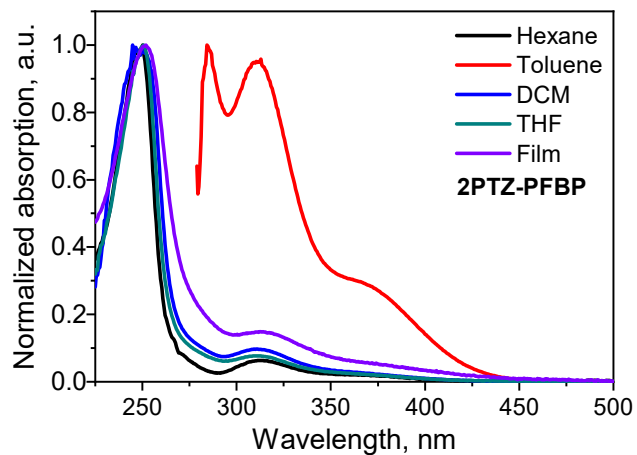
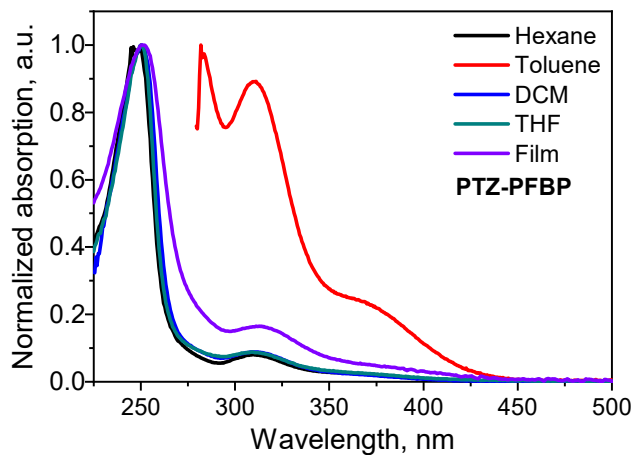


### Thermal characterization

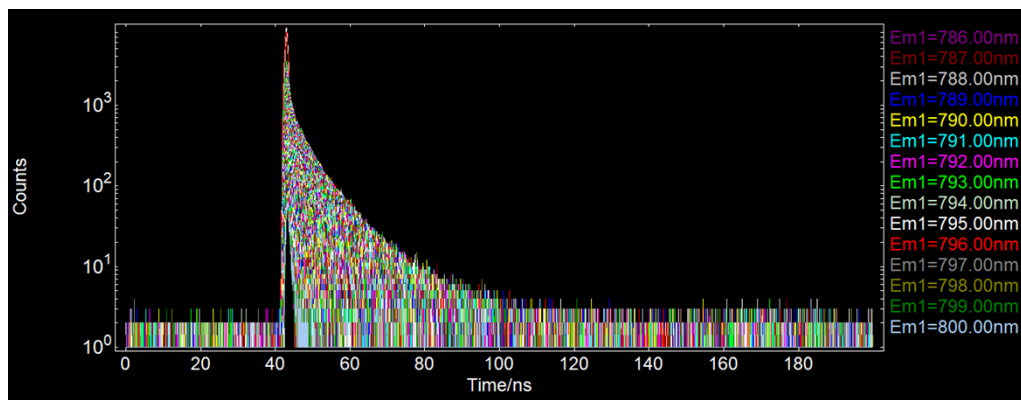


**Figure S1.** TGA (a) and DSC (b) curves of studied compounds

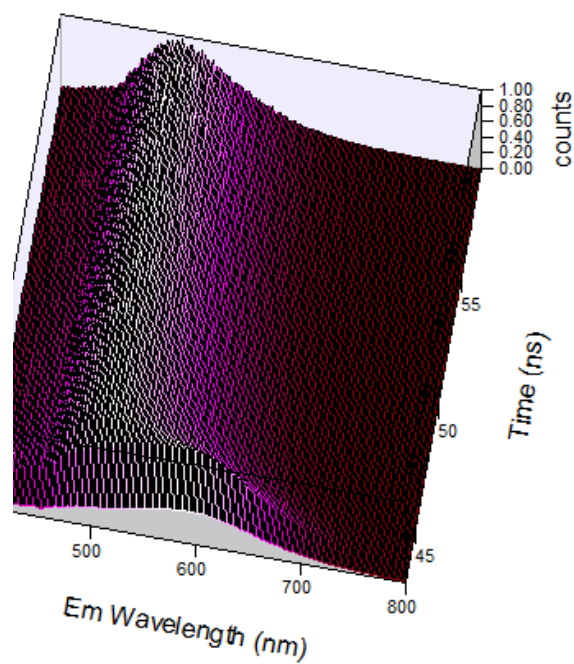
*Photophysical properties*



a)

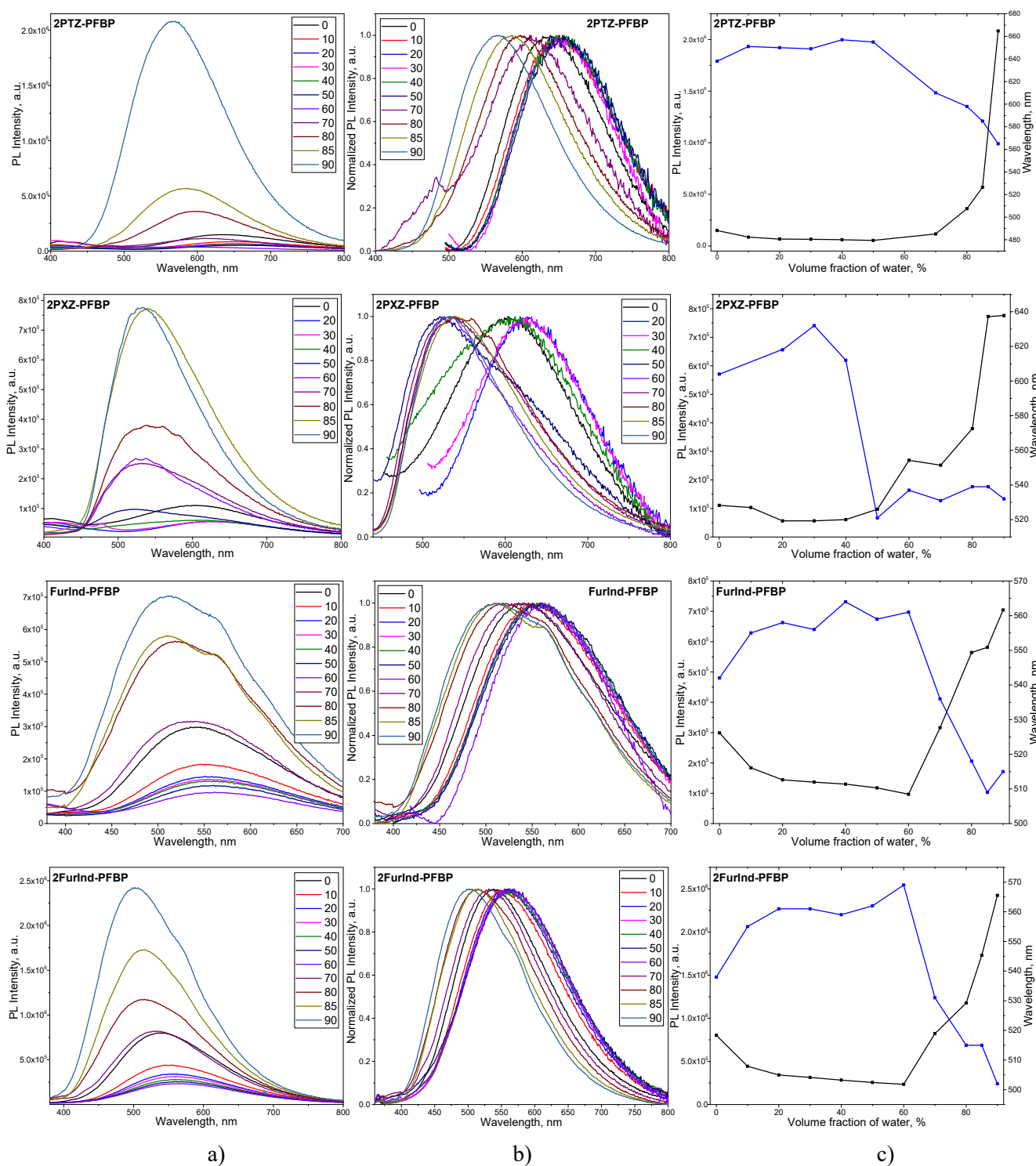


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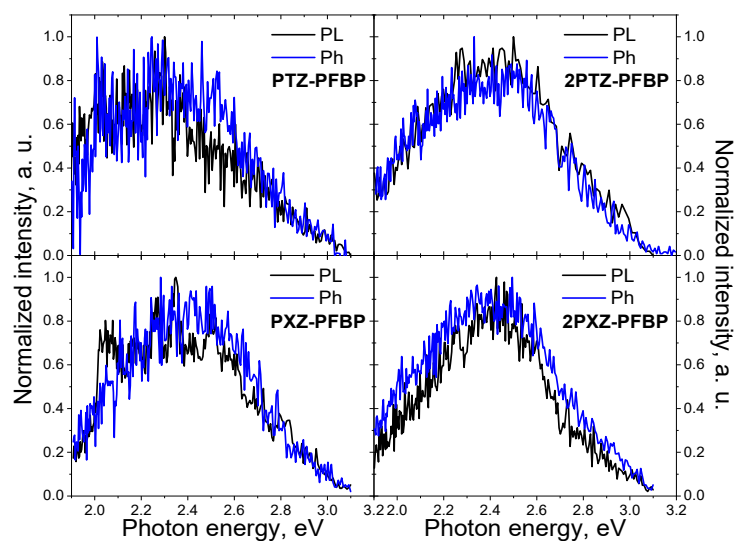


c)

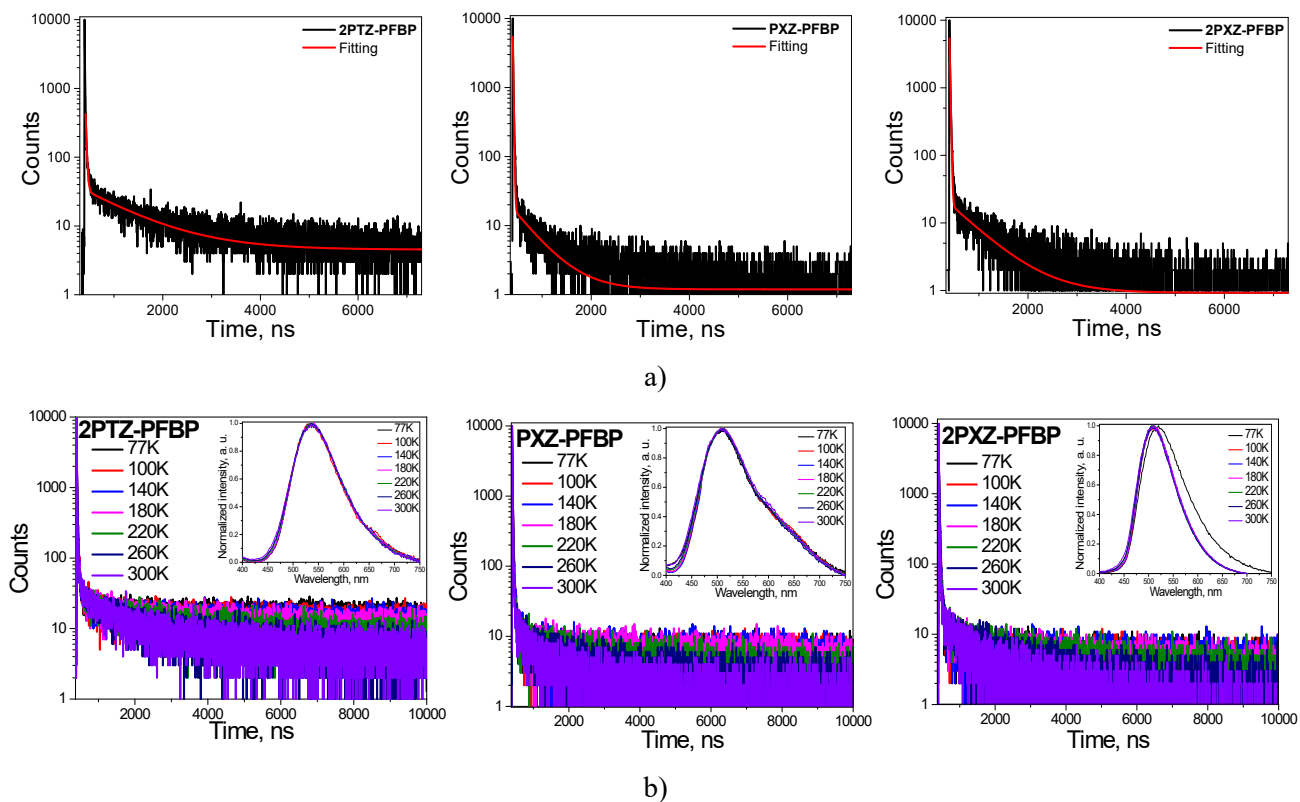
**Figure S2.** Absorption spectra (a) of dilute solution and of solid films of target compounds; PL decay curves (b) of THF solution of **PTZ-PFBP**; and non-normalized sliced PL spectra (c) of THF solution of **PTZ-PFBP** recorded at the different times after excitation.



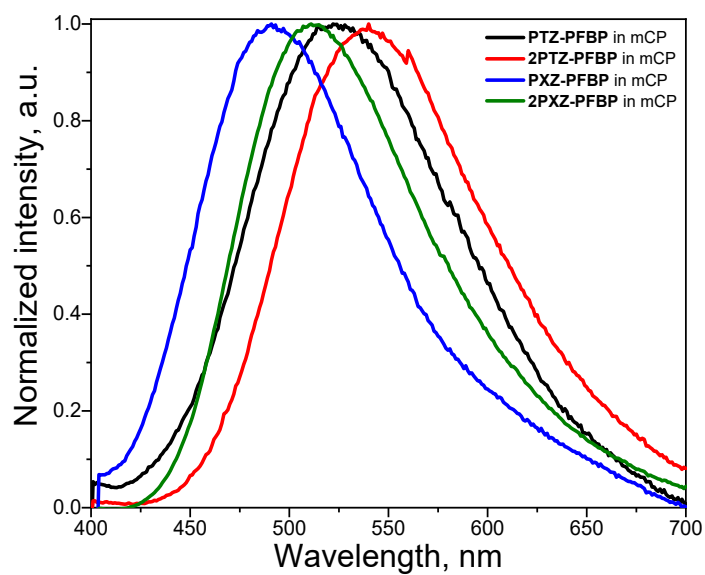
**Figure S3.** PL (a) and normalized PL spectra (b) and PL profiles (c) of the PFBP derivatives dispersed in THF/water mixtures with different amount of water



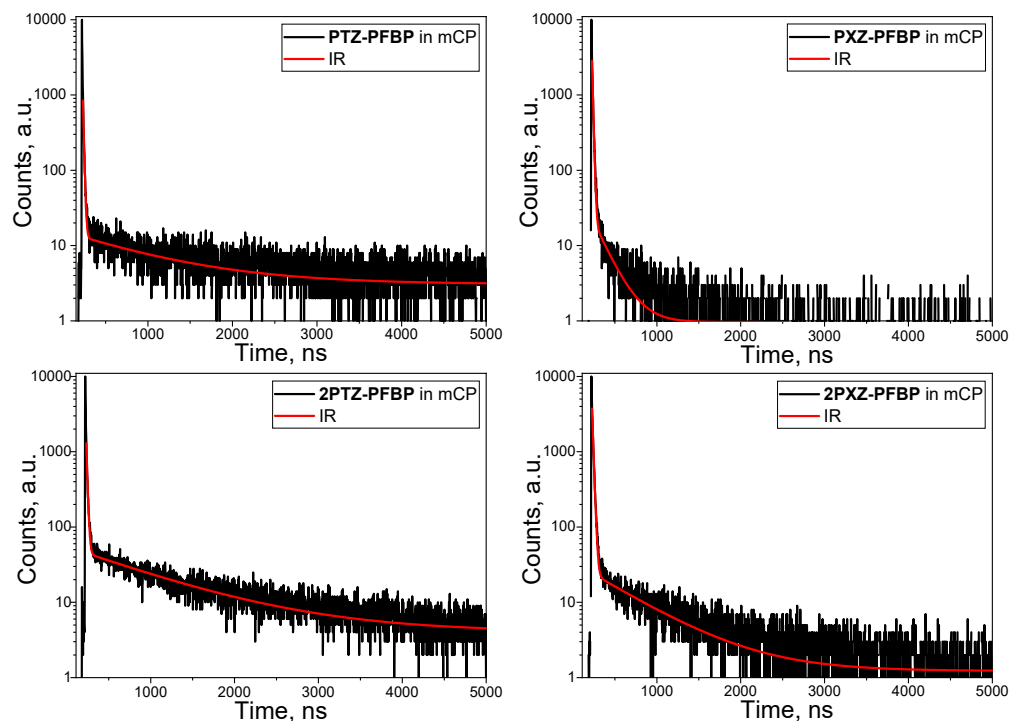
**Figure S4.** PL and Ph spectra of the PFBP derivatives in thin films at 77K



**Figure S5.** PL decay curves of films of **2PTZ-PFBP**, **PXZ-PFBP**, and **2PTZ-PFBP** at room (a) and at different (b) temperatures



a)



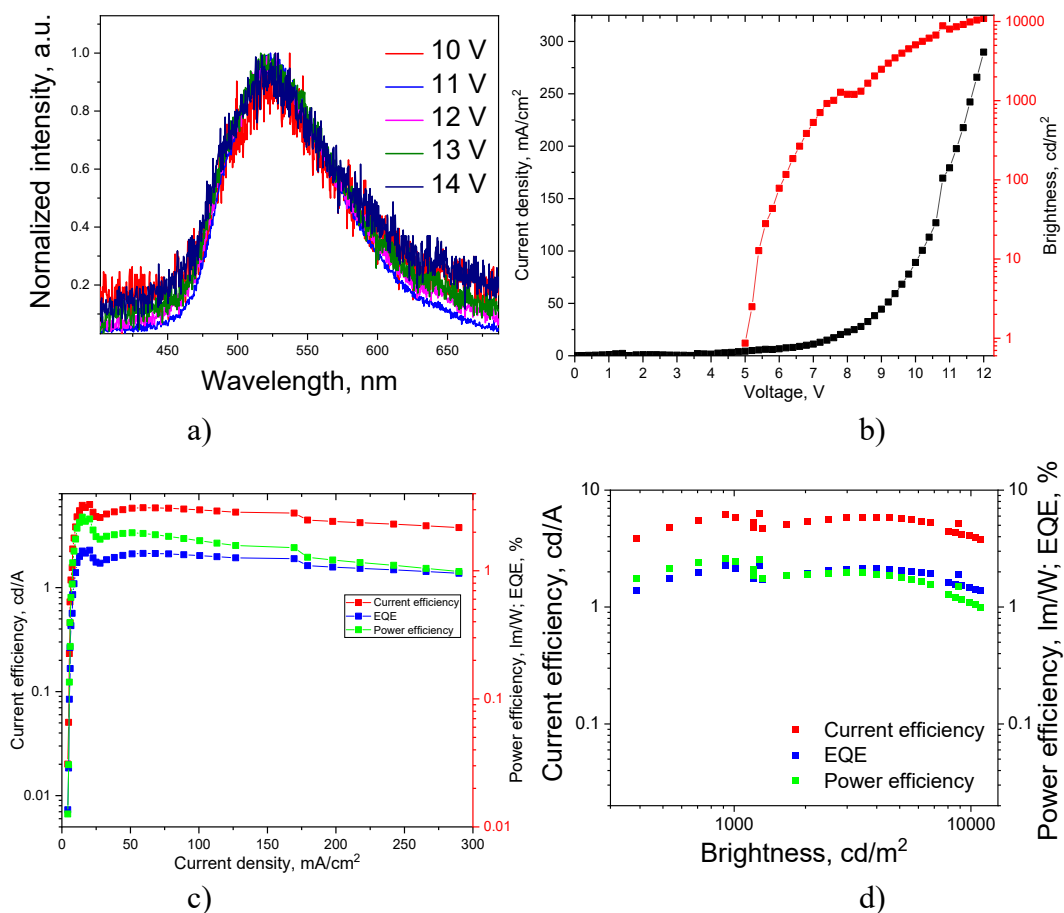
b)

**Figure S6.** Normalized PL spectra (a) and PL decay curves of the solid films of the molecular mixtures of 10% of PFBBs in mCP.

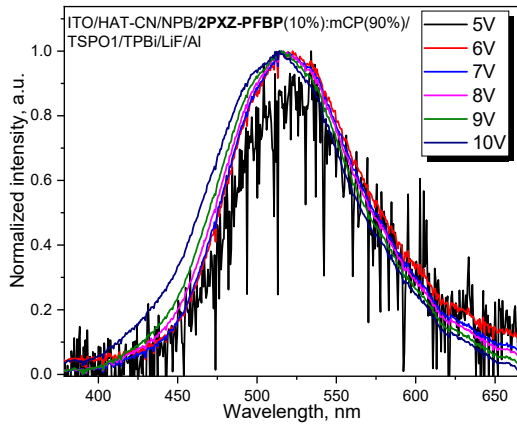


**Table S1.** PL characteristics of the solid films of the molecular mixtures of 10% of **PFBP**s in mCP

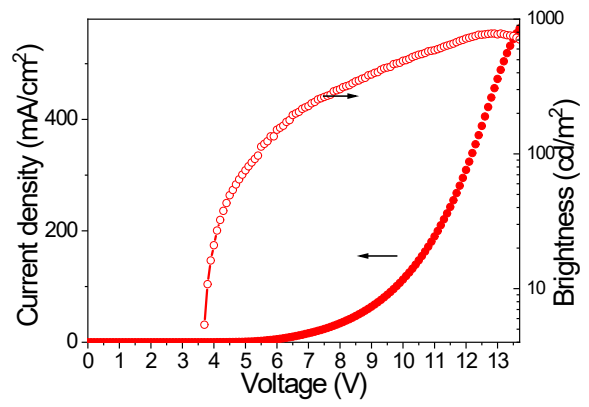
Compound	$\lambda_{\text{PL}}$ , nm	$\Phi_{\text{PL}}$
<b>PTZ-PFBP</b>	523	0.05
<b>2PTZ-PFBP</b>	540	0.15
<b>PXZ-PFBP</b>	491	0.17
<b>2PXZ-PFBP</b>	512	0.27



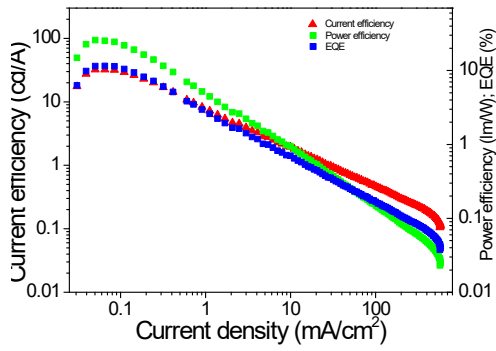
**Figure S7.** Normalized EL spectra (a), current density/voltage vs voltage graph (b) and current efficiency/power efficiency/EQE vs current density (c) and brightness (d) graph of A OLED.



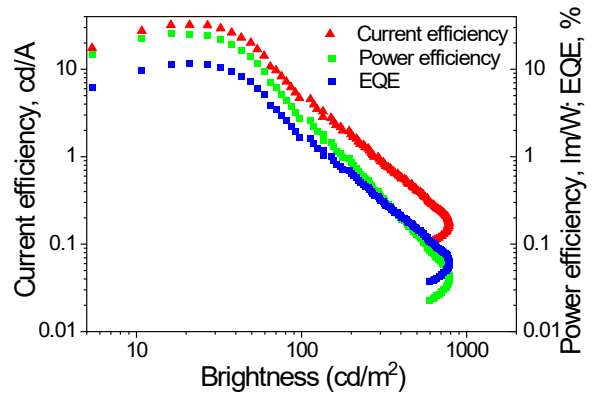
a)



b)



c)



d)

Normalized EL spectra (a), current density/voltage vs voltage graph (b) and current efficiency/power efficiency/EQE vs current density (c) and brightness (d) graph of B OLED.