

Supporting Information

Benzyl and Fluorinated Benzyl Side Chains for Perylene Diimide Non-Fullerene Acceptors

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- 1. Materials and Methods**
- 2. Synthetic Details**
- 3. ^1H , ^{13}C , ^{19}F NMR Spectra**
- 4. Mass Spectra**
- 5. Elemental Analysis**
- 6. Thermal Data**
- 7. Electrochemistry**
- 8. Optical Absorption Spectra**
- 9. Computational Analysis**
- 10. Thermal Annealing Study**
- 11. Organic Field Effect Transistors**
- 12. Organic Solar Cells**

1. Materials and Methods:

Materials: All reactants, reagents, and catalysts were purchased from Sigma-Aldrich. PTB7-Th was purchased from 1-Material. TTFQX-T1 (QX-1) was made by Yingping Zou's team as previously reported (J. Mater. Chem. A, 2018, **6**, 3074–3083). All solvents and materials purchased were used without further purification. Purification by flash column chromatography was performed using a Biotage® Isolera flash system.

Nuclear Magnetic Resonance (NMR): ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{19}F NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer at 300 K. Chemical shifts are reported in parts per million (ppm). Multiplicities are reported as: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), multiplet (m), quintet (quin), overlapping (ov), and broad (br).

High-resolution Mass Spectrometry (HRMS): High-resolution MALDI mass spectrometry measurements were performed courtesy of Jian Jun Li in the Chemical Instrumentation Facility at the University of Calgary. A Bruker Autoflex III Smartbeam MALDI-TOF (Na:YAG laser, 355nm), setting in positive reflective mode, was used to acquire spectra. Operation settings were all typical, e.g. laser offset 62-69; laser frequency 200Hz; and number of shots 300. The target used was Bruker MTP 384 ground steel plate target. Sample solution (~ 1 $\mu\text{g}/\text{mL}$ in dichloromethane) was mixed with matrix trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution (~ 5mg/mL in methanol). Pipetted 1 μl solution above to target spot and dried in the fume hood.

Cyclic Voltammetry (CV): All electrochemical measurements were performed using a Model 1200B Series Handheld Potentiostat by CH Instruments Inc. equipped with Ag wire, Pt wire and glassy carbon electrode, as the pseudo reference, counter electrode and working electrode respectively. Glassy carbon electrodes were polished with alumina. The cyclic voltammetry experiments were performed in anhydrous dichloromethane solution with ~0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at scan rate 100 mV/s. All electrochemical solutions were purged with dry N₂ for 5 minutes to deoxygenate the system. Solution CV measurements were carried out with a small molecule concentration of ~0.5 mg/mL in dichloromethane. The ionization potentials (IP) and electron affinities (EA) were estimated by correlating the $E_{1/2}$ values of the first of oxidation and reduction ($E_{\text{oxFc}/\text{Fc}^+}$, $E_{\text{redFc}/\text{Fc}^+}$) referenced to a ferrocene internal standard to that of the ionization potential of ferrocene using a conversion value of 4.8 (see: Advanced Materials, 1995, 7 (6), 551-554, Advanced Materials, 2011, 23 (20), 2367-2371).

UV-Visible Spectroscopy (UV-Vis): All optical absorption measurements were recorded using Agilent Technologies Cary 60 UV-Vis spectrometer at room temperature. All solution UV-Vis experiments were run in CHCl₃ using 10 mm quartz cuvettes. Films were spin-cast into Corning glass micro slides from CHCl₃ solutions (10 mg/mL) at 1500 rpm or from C₆H₅Cl solutions (10mg/mL) at 1500 rpm. Prior to use, glass slides were cleaned with soap and water, acetone and isopropanol, and followed by UV/ozone treatment using a Novascan UV/ozone cleaning system.

CHN Analysis: Elemental analysis was performed by Jian Jun Li in the Chemical Instrumentation Facility at the University of Calgary. A Perkin Elmer 2400 Series II CHN Elemental Analyzer was used to obtain CHN data from a minimum of 3 mg of sample with particle sizes ranging between 0.2 and 0.5 mm in diameter. Results were obtained in duplicate.

OTFT Fabrication: Bottom-gate, bottom-contact (BGBC) OTFTs were made using prefabricated Si/SiO₂ substrates with gold/indium tin oxide (ITO) source-drain contacts (L = 2.5 μm - 20 μm, W=2000 μm) manufactured by Fraunhofer IPMS. Substrates were rinsed with acetone, dried with nitrogen, and then treated with oxygen plasma for 15 minutes. These substrates were modified with octyltrichlorosilane (OTS, Sigma, 97%) in 1% v/v solution for 1 hour at 70 °C before rinsing and drying in vacuum at 70 °C for 1 hour. Spin cast devices were made using solutions of **1**, **2** and **3** in CHCl₃ (10 mg/mL) filtered with a 0.2 μm PTFE filter and deposited dynamically onto OTS-modified substrates spinning at 3000 rpm for 60s, producing consistent blue to purple films. The substrates were dried at 50 °C for 20 minutes under vacuum. After initial testing, devices were annealed in a vacuum chamber at 180 °C for 10 minutes and cooled to room temperature before re-testing.

OTFT Testing: Prepared OTFTs were transferred in an evacuated capsule into an OTFT testing chamber designed by Element Instrumentation. Devices were not exposed to air before testing around 0.5 Pa. Output and transfer characteristics were obtained for each device with L = 2.5 μm. For transfer curves, data was collected at V_{DS} = 70 V. The gate voltage range tested was 0 to 60V in all cases except for unannealed devices using **2**, which had a higher threshold voltage and required a range of 0V to 80V to fully capture transfer characteristics. The electron saturation field-effect mobility (μ_e) and threshold voltage (V_T) were calculated using the following equation, using the capacitance density (C_i) calculated from the dielectric thickness (t, 230 nm):

$$I_{DS} = \frac{\mu_e C_i W}{2L} (V_{GS} - V_T)^2$$

$$C_i = \frac{k\epsilon_0}{t}$$

where V_{GS} is the voltage applied between the gate and source, I_{DS} is the current measured between the source and drain, W and L are the channel width and length and k is the relative dielectric constant of SiO₂ (about 3.9).

OSC Fabrication/Testing: Devices were fabricated using ITO-coated glass substrates cleaned by sequentially ultra-sonicating detergent and de-ionized water, acetone, and isopropanol followed by exposure to UV/ozone for 30 minutes. ZnO was subsequently deposited as a sol-gel precursor solution in the air following the method of Sun et al.¹. The room temperature solution was filtered and spin-cast at a speed of 4000 rpm and then annealed at 200 °C in air for 15 min. Active layer solutions of PTB7-Th and **PDI** material **1**, **2**, and **3** were prepared in the air with a total concentration of 10 mg/mL in CB. Solutions of PTB7-Th was stirred at 70 °C for 4-6 hrs. Active layer materials were combined in a 1:1 D/A weight ratio and cast at room temperature at a speed of 1500 rpm for 60 seconds. Active layer solutions of QX1(TTFQx-T1) and **PDI** material **1**, **2**, and **3** were prepared in the air with a total concentration of 10 mg/mL in 2Me-THF. Active layer materials were combined in a 4:6 D/A weight ratio and cast at room temperature at a speed of 1500 rpm for 60 seconds. All substrates upon casting active layers were kept in an N₂ atmosphere glovebox overnight before evaporating MoO_x and Ag. The evaporation of 10 nm of MoO_x followed by 100 nm of Ag was thermally deposited under vacuum (3x10⁻⁶ Torr). The active

areas of resulting devices were 0.09 cm^2 . The current density-voltage (J-V) curves were measured by a Keithley 2420 source measure unit. The photocurrent was measured under AM 1.5 illumination at 100 mW/cm^2 under a Solar Simulator (Newport 92251A-1000). The standard silicon solar cell (Newport 91150V) was used to calibrate light intensity. All tests carried out in air.

2. Synthetic Details:

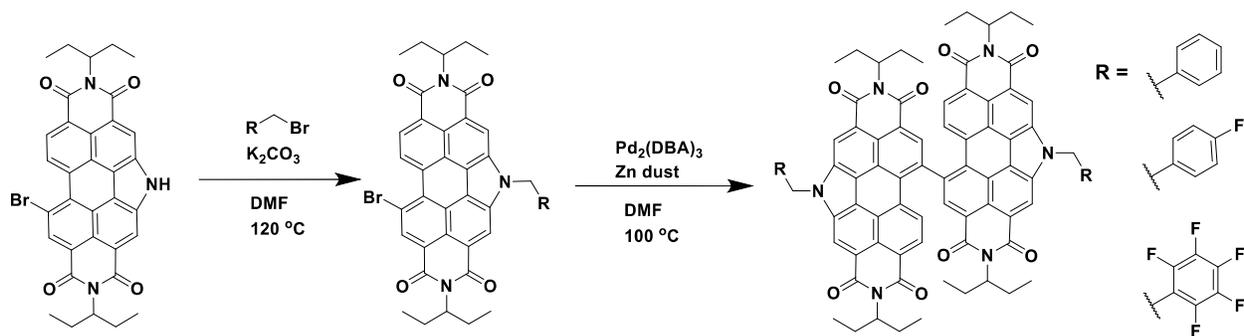
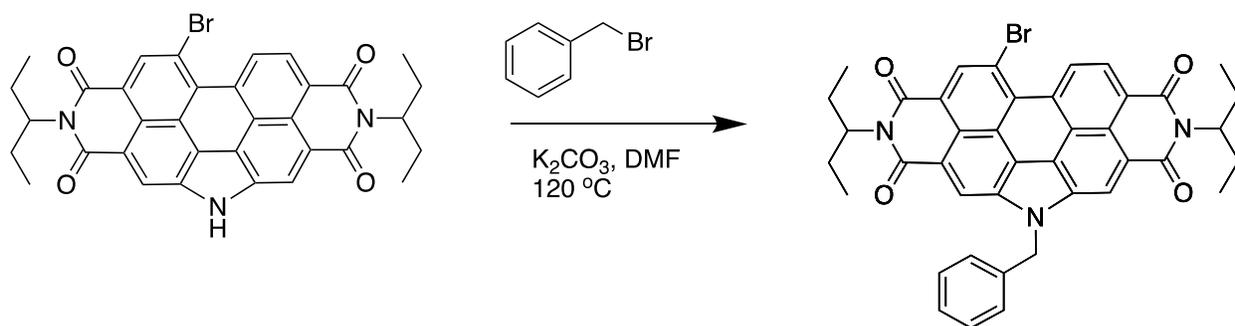


Figure S1. Synthesis of the target PDI materials.

Synthesis of Br-PDIN-benzyl:



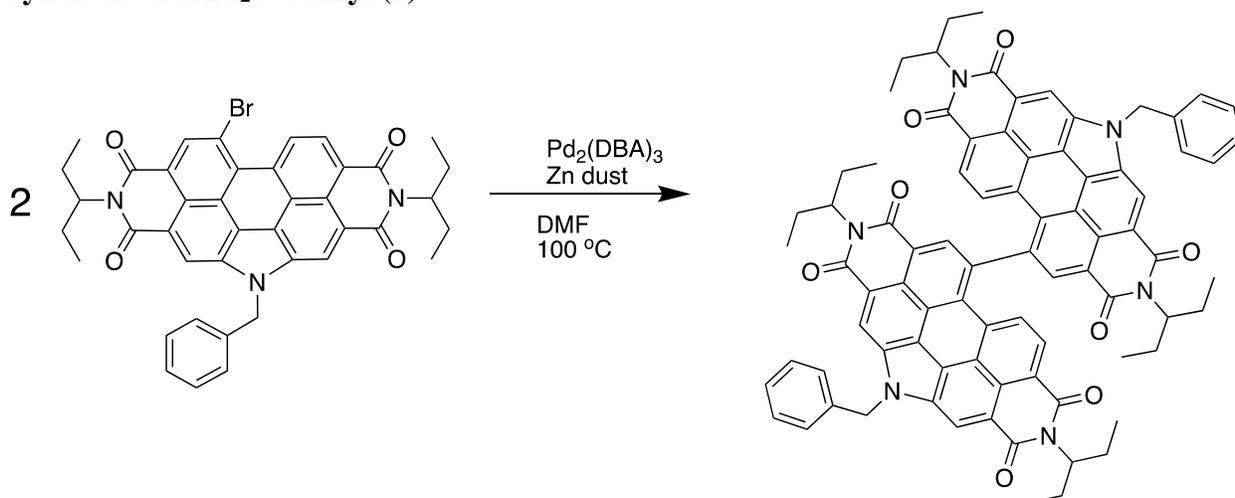
In a two-neck 250 mL round bottom flask were transferred Br-PDIN-H (1.3 g, 2.09 mmol) and K_2CO_3 (0.578 g, 4.18 mmol) along with a stir-bar. The flask was fitted with a reflux condenser, sealed, and then purged with nitrogen for 10 minutes. Approximately 60 mL of dry *N,N*-dimethylformamide were added via canula transfer. Benzyl-bromide (0.537 g, 3.14 mmol) was added to the flask via syringe and the reaction mixture was placed in a LabArmor® bead bath and heated at $120\text{ }^\circ\text{C}$ for 35 minutes, at which time TLC analysis showed reaction completion. The reaction was taken up in 200 mL of methanol and 30 mL of water and left to stir for 1 hour. Crude solid was recovered *via* vacuum filtration, washing with methanol. The solid was recrystallized by dissolving in a minimal amount of dichloromethane and precipitating with methanol. **Yield:** 1.3011 g (87%)

$^1\text{H-NMR}$ (500 MHz, chloroform-*d*) δ : 10.06-10.02 (d, 1H), 8.96 (s 1H), 8.93-8.90 (d, 2H), 8.80 (s, 1H), 7.35-7.30 (m, 3H), 7.29-7.26 (m, 2H), 6.05 (s, 2H), 5.24-5.14 (m, 2H), 2.41-2.29 (m, 5H), 2.09-1.98 (m, 5H), 1.03-0.968 (q, 14H)

$^{13}\text{C-NMR}$ (125 MHz, chloroform-*d*) δ : 135.50, 134.17, 133.96, 128.78, 128.17, 127.08, 126.49, 123.73, 123.15, 122.79, 121.62, 120.99, 118.50, 118.06, 57.49, 57.35, 49.71, 24.63, 24.57, 10.98, 10.94

MALDI-TOF: *m/z* expected: 712.63 obtained: 712.1827

Synthesis of tPDI₂N-benzyl (1):



In a 20 mL pressure vial was transferred Br-PDIN-benzyl (500 mg, 0.702 mmol) and zinc dust (200 mg, 3.51 mmol). Tris(dibenzylideneacetone)dipalladium(0) (64 mg 10 mol%) was added under N₂ in the glovebox and the vial was sealed with a Teflon® cap. Out of the glovebox 15 mL of anhydrous *N,N*-dimethylformamide were added *via* syringe, The vial was placed in a LabArmor® bead bath heated at 100 °C for 25 minutes, after which the solution turned blue and TLC analysis showed reaction completion. The reaction mixture was extracted with dichloromethane and passed through a silica plug to remove the zinc and palladium catalyst. The solution was then concentrated and passed through a second silica plug to ensure total remove of zinc and palladium catalyst. The dichloromethane was removed *via* rotary evaporation and the crude solid was isolated *via* precipitation from methanol. The solid was purified by boiling in isopropanol for 1.5 hours. The isolated solid was then re-dissolved in dichloromethane and slurried with Celite 545 and aluminum oxide for 1 hour. The slurry was vacuum filtered, the solvent was removed, and the solid was isolated *via* vacuum filtration following precipitation from methanol. **Yield:** 263 mg (59%).

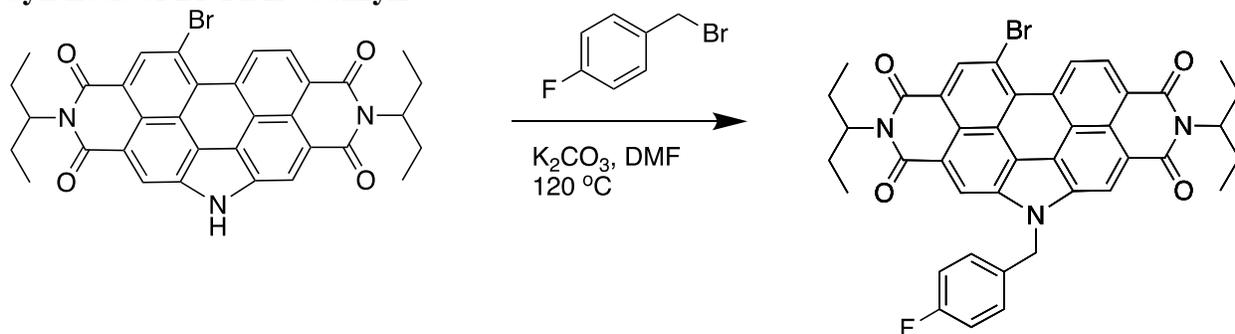
¹H-NMR (500 MHz, chloroform-d) δ: 9.21 (s, 1H), 9.04 (s, 1H), 8.87 (s, 1H), 8.00-7.96 (d, 1H), 7.72-7.70 (d, 1H), 7.48-7.37 (m, 6H), 6.20 (s, 2H), 5.21 (bs, 1H), 5.02 (bs, 1H), 2.40-2.28 (m, 2H), 2.24-2.12 (m, 2H), 2.05-1.93 (m, 2H), 1.90-1.79 (m, 2H), 1.02-0.979 (t, 7H) and 0.819 (bs, 7H)

¹³C-NMR (125 MHz, chloroform-d) δ: 141.03, 136.26, 135.53, 135.32, 133.57, 130.57, 129.59, 128.93, 127.37, 127.04, 125.20, 124.95, 123.67, 122.86, 120.46, 120.15, 58.13, 57.74, 50.69, 25.30, 25.13, 11.66, 11.39.

MALDI-TOF: m/z expected:1264.51 obtained:1264.5043.

Elemental Analysis: Theory %C 77.83, %H 5.42, %N 6.64. Actual %C 76.36, %H 5.55, %N 6.64.

Synthesis of Br-PDIN-benzylF:



In a two-neck 250 mL round bottom flask was transferred Br-PDIN-H (1.3867 g, 2.23 mmol) and K_2CO_3 (0.616 g, 4.46 mmol). The flask was fitted with a reflux condenser, sealed, and then purged with nitrogen for 10 minutes. Approximately 60 mL of dry *N,N*-dimethylformamide was added *via* canula transfer. Para-fluorobenzylbromide (0.631 g, 3.34 mmol) was added to the flask *via* syringe and the reaction mixture was placed in a LabArmor® bead bath and heated at $120\text{ }^\circ\text{C}$ for 1 hour and 20 minutes, at which time TLC analysis showed reaction completion. The reaction was taken up in 200 mL of methanol and 30 mL of water and left to stir for 1 hour. Crude solid was recovered *via* vacuum filtration, washing with methanol. The solid was recrystallized by dissolving in a minimal amount of dichloromethane and precipitating with methanol. **Yield:** 1.34 g (82%)

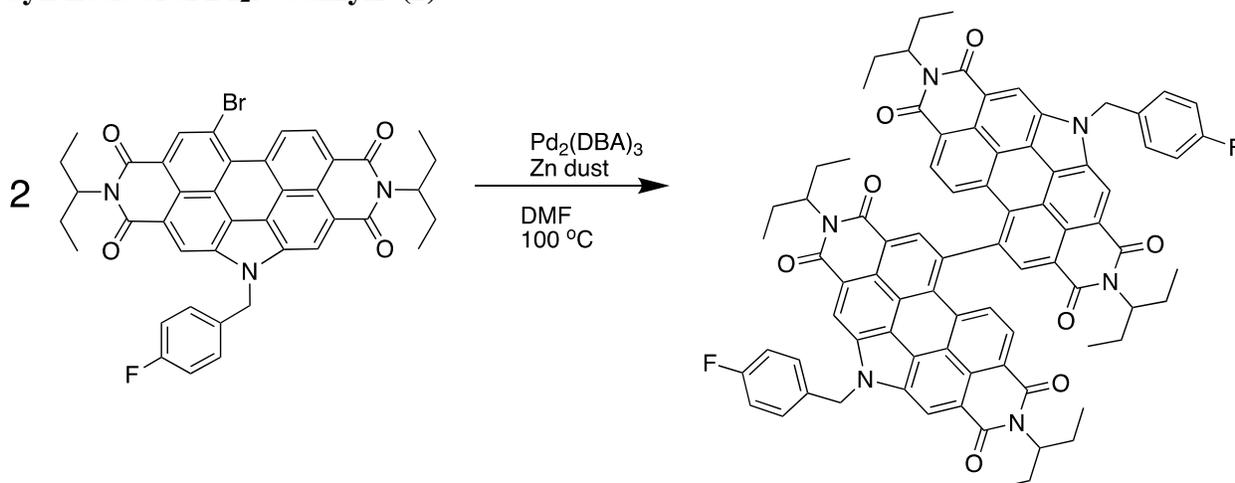
$^1\text{H-NMR}$ (500 MHz, chloroform-*d*) δ : 10.16-10.11 (d, 1H), 9.02 (s, 1H), 8.95-8.91 (d, 2H), 8.86-8.82 (d, 1H), 7.32-7.26 (m, 2H), 7.05-7.00 (t, 2H), 6.04 (s, 2H), 5.25-5.13 (m, 2H) 2.42-2.27 (m, 4H), 2.10-1.96 (m, 4H), 1.03-0.954 (q, 13H)

$^{13}\text{C-NMR}$ (125 MHz, chloroform-*d*) δ : 134.05, 133.81, 131.97, 131.14, 129.99, 128.31, 128.24, 127.14, 123.75, 123.15, 122.79, 121.63, 121.08, 118.53, 118.11, 115.95, 115.75, 57.52, 57.38, 49.07, 24.61, 11.04

$^{19}\text{F-NMR}$ (390 MHz, chloroform-*d*) δ : 113.60 (s)

MALDI-TOF: *m/z* expected: 730.63 obtained: 730.1680

Synthesis of tPDI₂N-benzylF (2):



In a 20 mL pressure vial was transferred Br-PDIN-benzylF (511.8 mg, 0.700 mmol) and zinc dust (229 mg, 3.50 mmol). Tris(dibenzylideneacetone)dipalladium(0) (64 mg, 10 mol%) was added under N₂ in the glovebox and the vial was sealed with a Teflon® cap. Out of the glovebox 15 mL of anhydrous *N,N*-dimethylformamide was added *via* syringe. The vial was placed in a LabArmor® bead bath and heated at 100 °C for 1 hour and 10 minutes, after which the solution turned purple and TLC analysis showed reaction completion. The reaction mixture was extracted with dichloromethane and passed through a silica plug to remove zinc and palladium catalyst. The solution was then concentrated and passed through a second silica plug to ensure total remove of zinc and catalyst. The dichloromethane was removed *via* rotary evaporation and the crude solid was isolated *via* precipitation from methanol. The solid was purified by in boiling isopropanol for 1.5 hours. The isolated solid was then redissolved in dichloromethane and slurried with Celite 545 and aluminum oxide for 1 hour. The slurry was vacuum filtered, the solvent was removed, and the solid was isolated *via* vacuum filtration following precipitation from methanol. **Yield:** 263.9 mg (58%).

¹H-NMR (500 MHz, chloroform-*d*) δ: 9.20 (s, 1H), 9.03 (s, 1H), 8.88 (s, 1H), 8.01-7.96 (d, 1H), 7.73-7.70 (d, 1H), 7.47-7.42 (dd, 2H), 7.15-7.09 (t, 2H), 6.18 (s, 2H), 5.21 (bs, 1H), 5.03 (bs, 1H), 2.39-2.29 (m, 2H), 2.22-2.12 (m, 2H), 2.04-1.94 (m, 2H), 1.90-1.80 (m, 2H), 1.03-0.974 (t, 6H), 0.820 (bs, 6H)

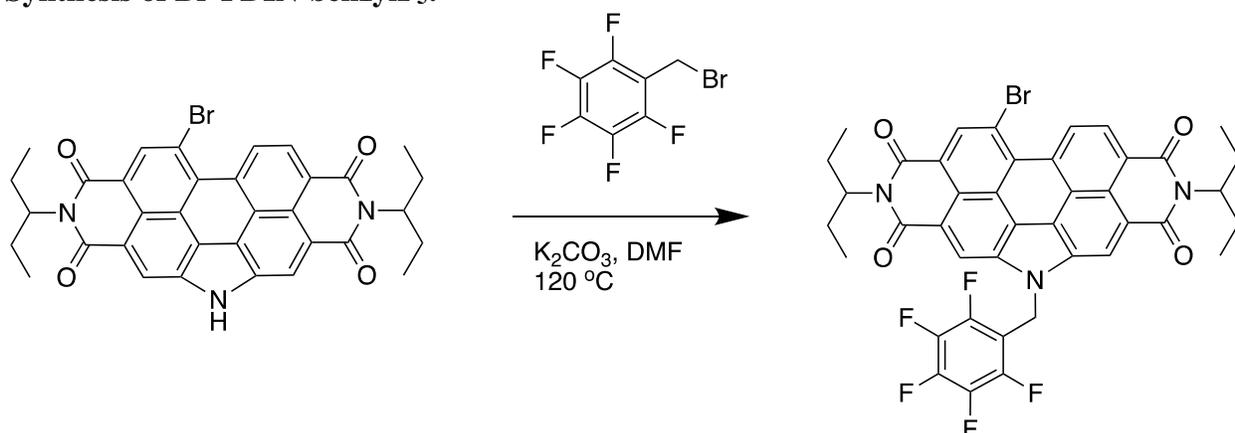
¹³C-NMR (125 MHz, chloroform-*d*) δ: 163.21, 161.24, 140.35, 134.70, 134.49, 132.37, 131.42, 131.39, 129.88, 128.50, 128.44, 126.39, 124.51, 124.26, 123.0, 122.17, 119.80, 119.50, 118.42, 116.04, 115.86, 57.48, 57.09, 49.28, 24.61, 24.44, 10.96, 10.69

¹⁹F-NMR (390 MHz, chloroform-*d*) δ: -112.90 (s)

MALDI-TOF: *m/z* expected:1300.49 obtained:1300.4904.

Elemental Analysis: Theory %C 75.68, %H 5.11, %N 6.46. Actual %C 74.94, %H 5.11, %N 6.27.

Synthesis of Br-PDIN-benzylF₅:



In a two-neck 250 mL round bottom flask was transferred Br-PDIN-H (0.9688 g, 1.782 mmol) and K₂CO₃ (0.4926 g, 3.564 mmol). The flask was fitted with a reflux condenser, sealed, and then purged with nitrogen for 10 minutes. Approximately 60 mL of dry *N,N*-dimethylformamide was added *via* canula transfer. Pentafluorobenzylbromide (0.6977 g, 2.673 mmol) was added to the flask *via* syringe and the reaction mixture was placed in a LabArmor® bead bath and heated at 120 °C for 3 hours, at which time TLC analysis showed reaction completion. The reaction was taken up in 200 mL of methanol and 30 mL of water and left to stir for 1 hour. The crude solid was loaded on silica gel and purified using column chromatography, eluting with 100% dichloromethane. The solvent was removed using a rotary evaporator and the solid isolated *via* vacuum filtration following precipitation from methanol. **Yield:** 0.9045 g (70%)

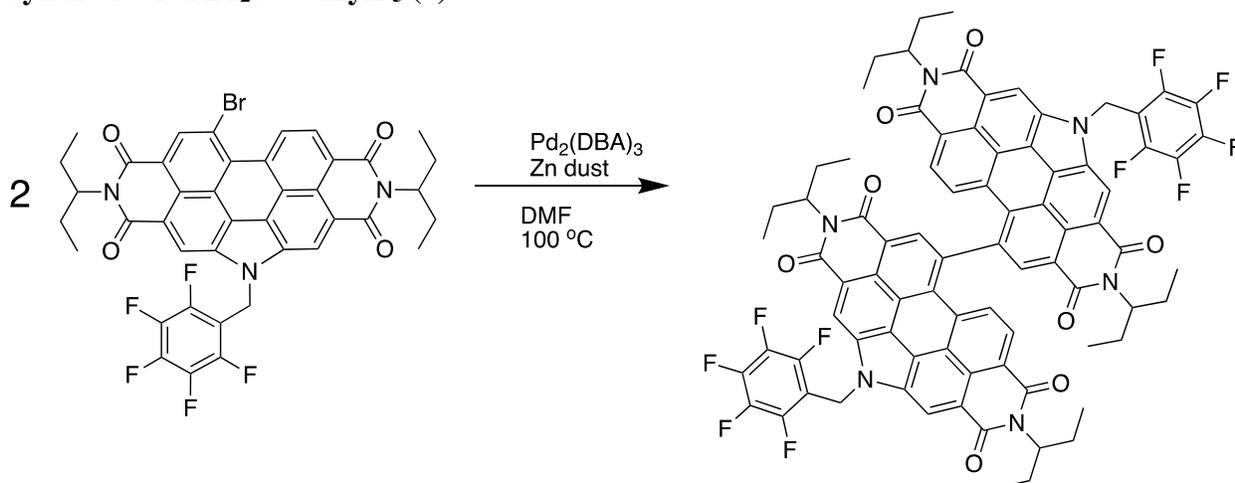
¹H-NMR (500 MHz, chloroform-d) δ : 10.28-10.24 (d, 1H), 9.17-9.12 (d, 2H), 9.09-9.06 (s, 1H), 8.93-8.86 (s, 1H), 6.20 (s, 2H), 5.26-5.16 (m, 2H), 2.42-2.30 (m, 4H), 2.09-1.97 (m, 4H), 1.02-0.961 (q, 13H)

¹³C-NMR (125 MHz, chloroform-d) δ : 145.88, 143.90, 142.63, 138.41, 136.34, 133.52, 131.02, 129.08, 126.38, 122.33, 121.74, 120.73, 117.94, 116.67, 108.82, 57.61, 36.87, 24.60, 11.08

¹⁹F-NMR (390 MHz, chloroform-d) δ : -141.60-141.68 (d), -151.45-151.62 (t), -159.79-159.99 (t)

MALDI-TOF: m/z expected:802.60 obtained:802.1343

Synthesis of tPDI₂N-benzylF₅ (3):



In a 20 mL pressure vial was transferred Br-PDIN-benzylF₅ (388.4 mg, 0.4216 mmol) and zinc dust (137.8 mg, 3.156 mmol). Tris(dibenzylideneacetone)dipalladium(0) (38.6 mg, 10 mol%) was added under N₂ in the glovebox and the vial was sealed with a Teflon® cap. Out of the glovebox 15 mL of anhydrous *N,N*-dimethylformamide was added *via* syringe. The vial was placed in a LabArmor® bead bath and heated at 100 °C for 1 hour and 40 minutes, after which the solution turned dark brown and TLC analysis showed reaction completion. The reaction mixture was extracted with dichloromethane and passed through a silica plug to remove zinc and palladium catalyst. The solution was then concentrated and passed through a second silica plug to ensure total remove of zinc and catalyst. The dichloromethane was removed *via* rotary evaporation and the crude solid was isolated *via* precipitation from methanol. The crude solid was loaded on silica gel and purified using column chromatography (100% dichloromethane). The solvent was removed using a rotary evaporator then slurried with Celite 545 and aluminum oxide for 1 hour. The slurry was vacuum filtered, the solvent was removed and the solid was isolated *via* vacuum filtration following precipitation from methanol. **Yield:** 179.6 mg (59%)

¹H-NMR (500 MHz, chloroform-*d*) δ: 9.36 (s, 1H), 9.17 (s, 1H), 8.88 (s, 1H), 7.96 (d, 1H), 7.67-7.64 (d, 1H), 6.29 (s, 2H), 5.22 (bs, 1H), 5.03 (bs, 1H), 2.37 (s, 2H), 2.19 (s, 2H), 2.06-1.97 (m, 2H), 1.92-1.82 (m, 2H), 1.05-0.984 (t, 7H), 0.827 (bs, 8H)

¹³C-NMR (125 MHz, chloroform-*d*) δ: 140.30, 134.47, 134.24, 132.36, 129.89, 126.39, 126.39, 124.57, 124.30, 122.91, 122.06, 119.90, 119.58, 57.55, 57.15, 37.07, 30.38, 29.13, 24.60, 24.42, 10.97, 10.70

¹⁹F-NMR (390 MHz, chloroform-*d*) δ: -141.40-141.58 (d), -151.41-151.55 (t), -159.67-159.85 (td)

MALDI-TOF: *m/z* expected: 1443.41 obtained: 1444.4129.

Elemental Analysis: Theory %C 68.14, %H 4.04, %N 5.81. Actual %C 68.04, %H 4.17, %N 5.69.

3. ^1H , ^{13}C , and ^{19}F NMR Spectra:

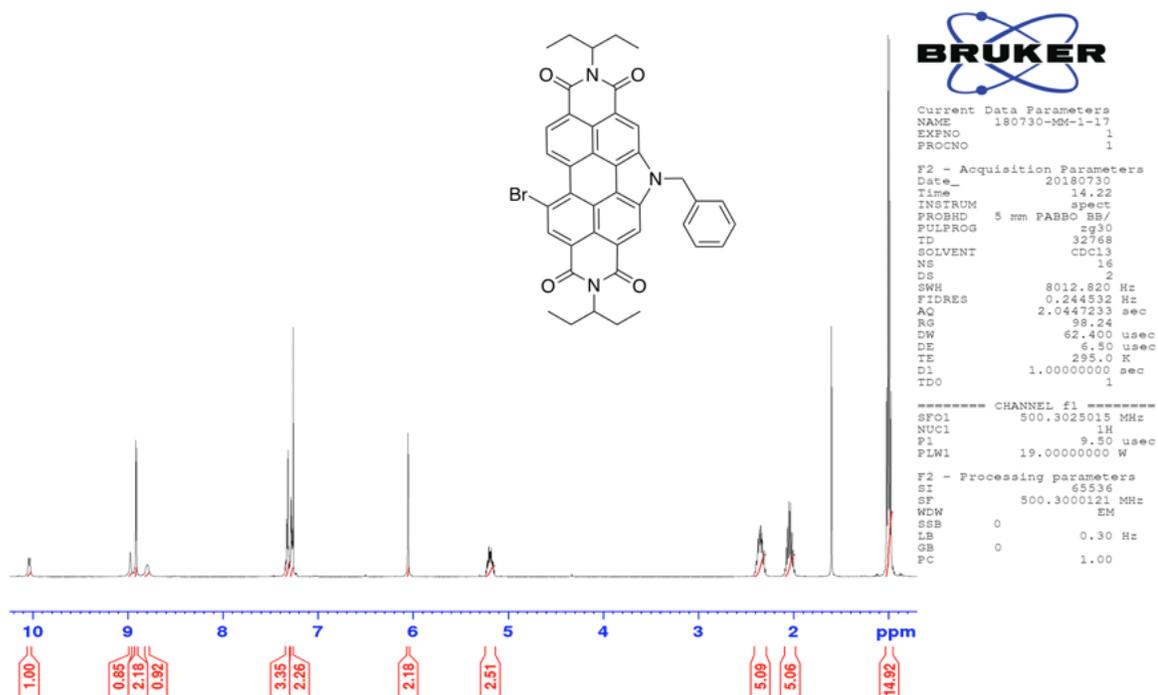


Figure S2: ^1H -NMR spectrum of Br-PDIN-benzyl in CDCl_3 .

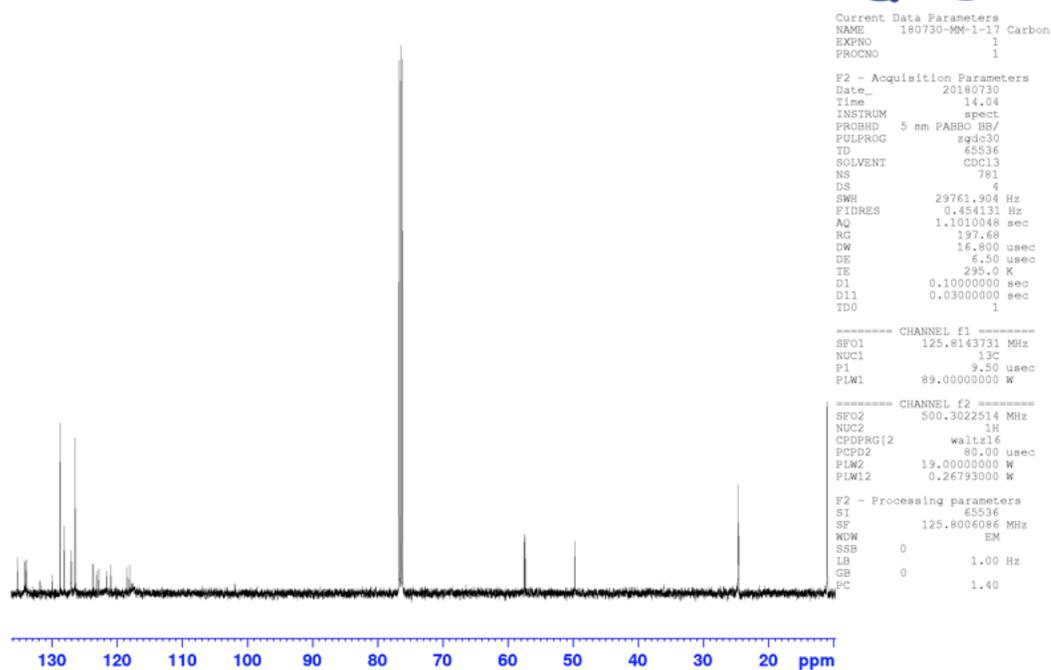


Figure S3: ^{13}C -NMR spectrum of Br-PDIN-benzyl in CDCl_3 .

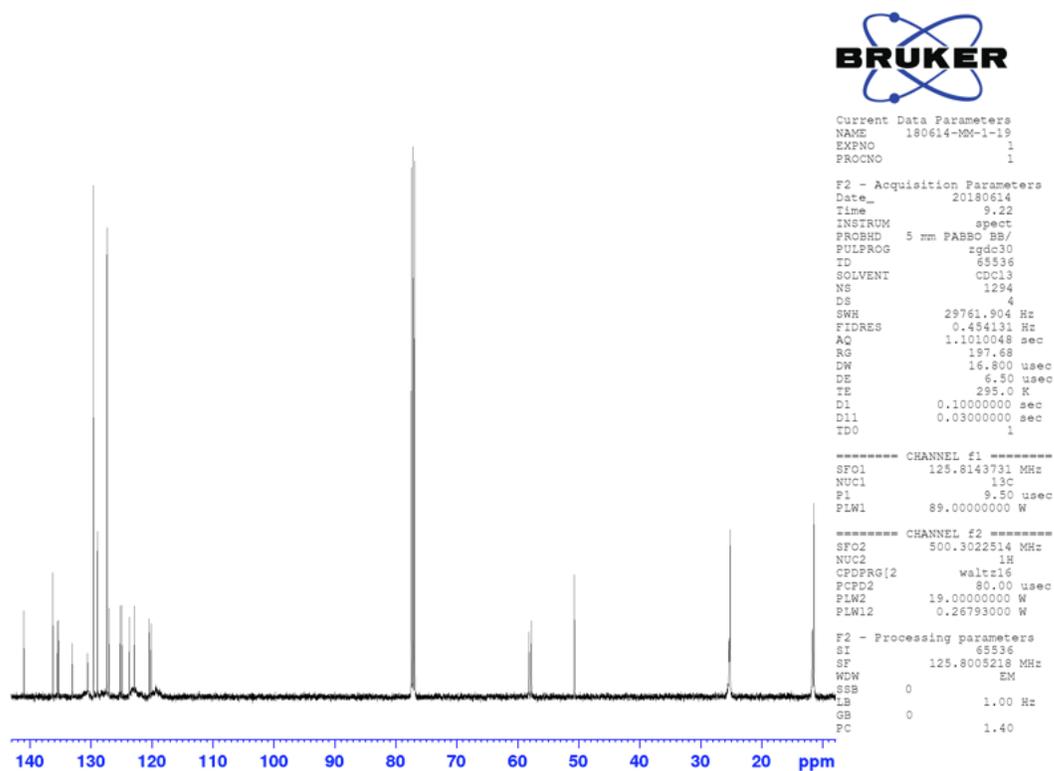


Figure S5: ^{13}C -NMR spectrum of (1) tPDI₂N-benzyl in CDCl₃.

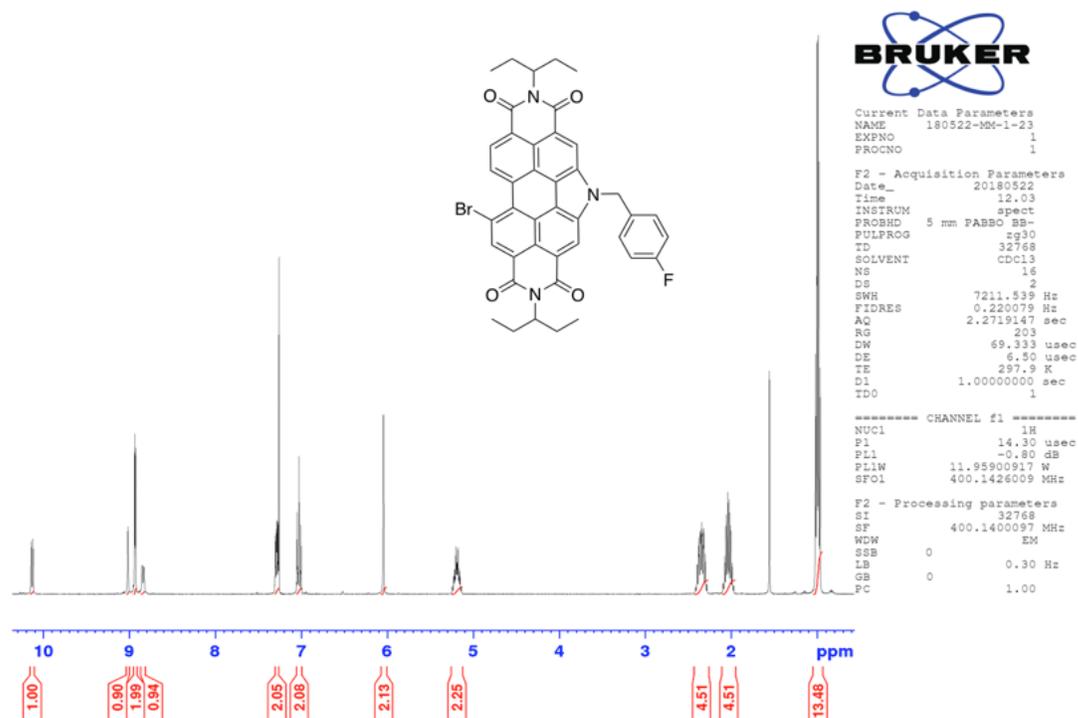
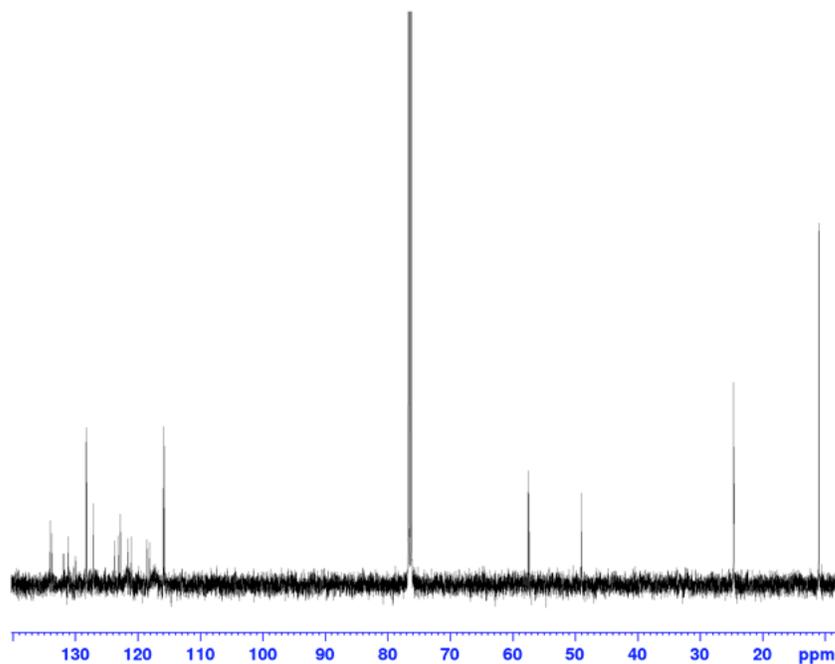


Figure S6: ^1H -NMR spectrum of Br-PDIN-benzylF in CDCl_3 .



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EXPNO 1
PROCNO 1

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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
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DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
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TE 295.0 K
D1 0.10000000 sec
D11 0.03000000 sec
TDO 1

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NUC1 13C
P1 9.50 usec
PLW1 89.00000000 W

----- CHANNEL f2 -----
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NUC2 1H
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PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.26793000 W

F2 - Processing parameters
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Figure S7: ^{13}C -NMR spectrum of Br-PDIN-benzylF in CDCl_3 .

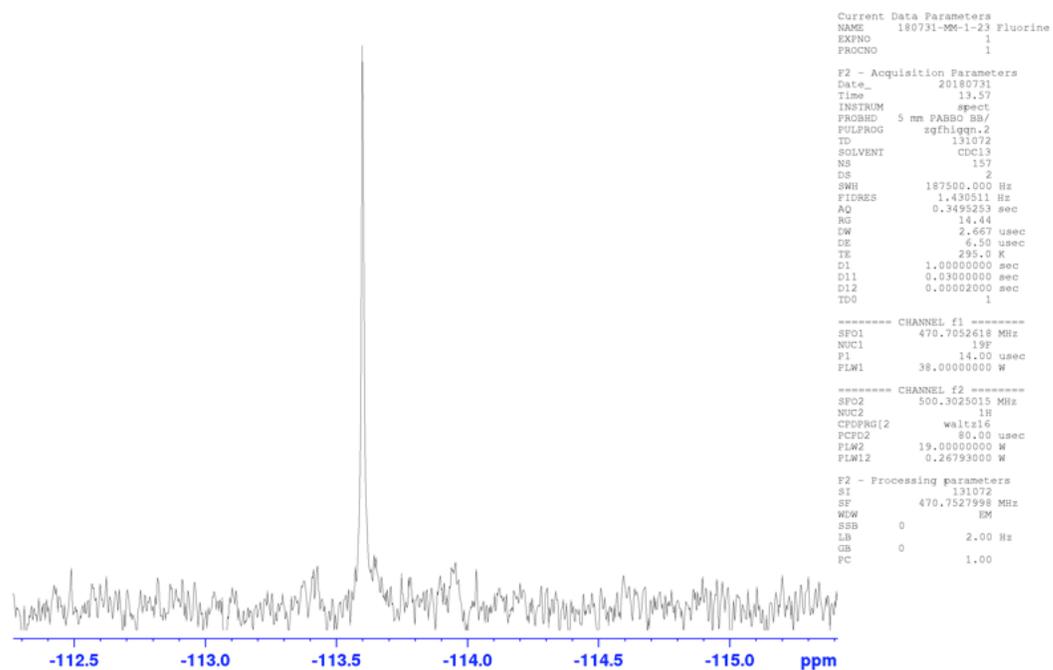


Figure S8: ^{19}F -NMR spectrum of Br-PDIN-benzylF in CDCl_3 .

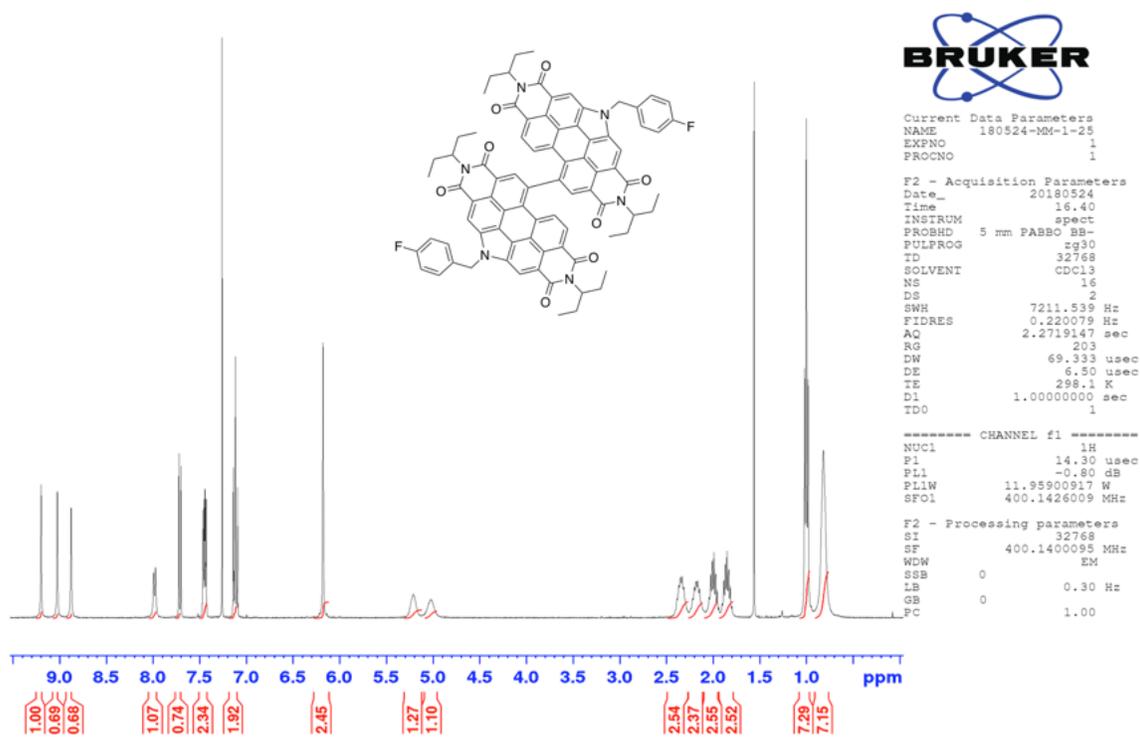


Figure S9: ¹H-NMR spectrum of (2) tPDI₂N-benzylF in CDCl₃.

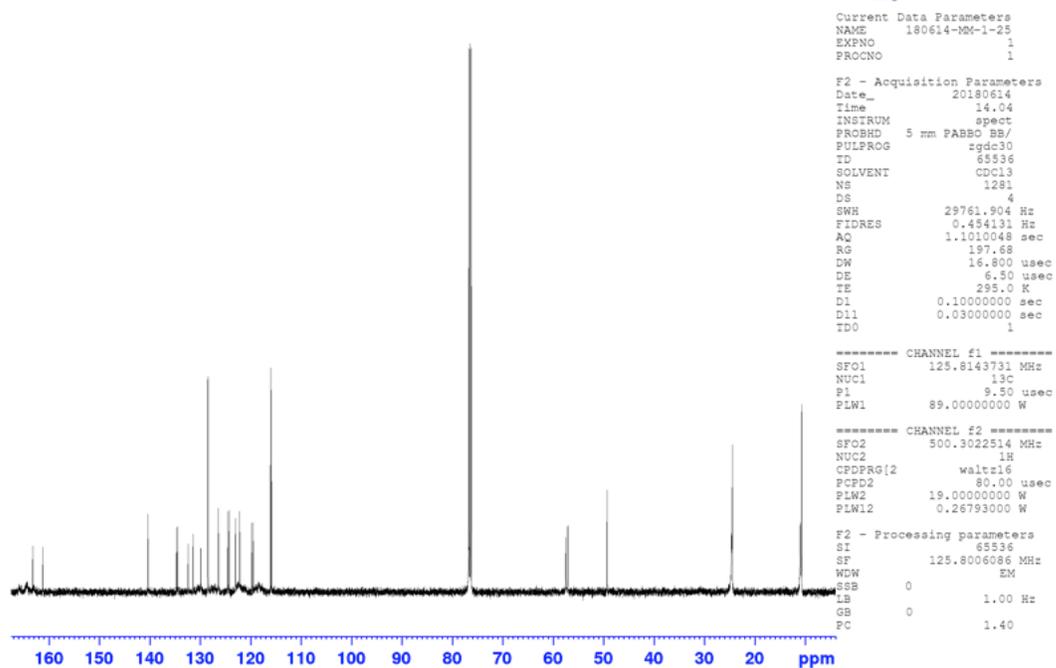


Figure S10: ^{13}C -NMR spectrum of (2) tPDI₂N-benzylF in CDCl₃.

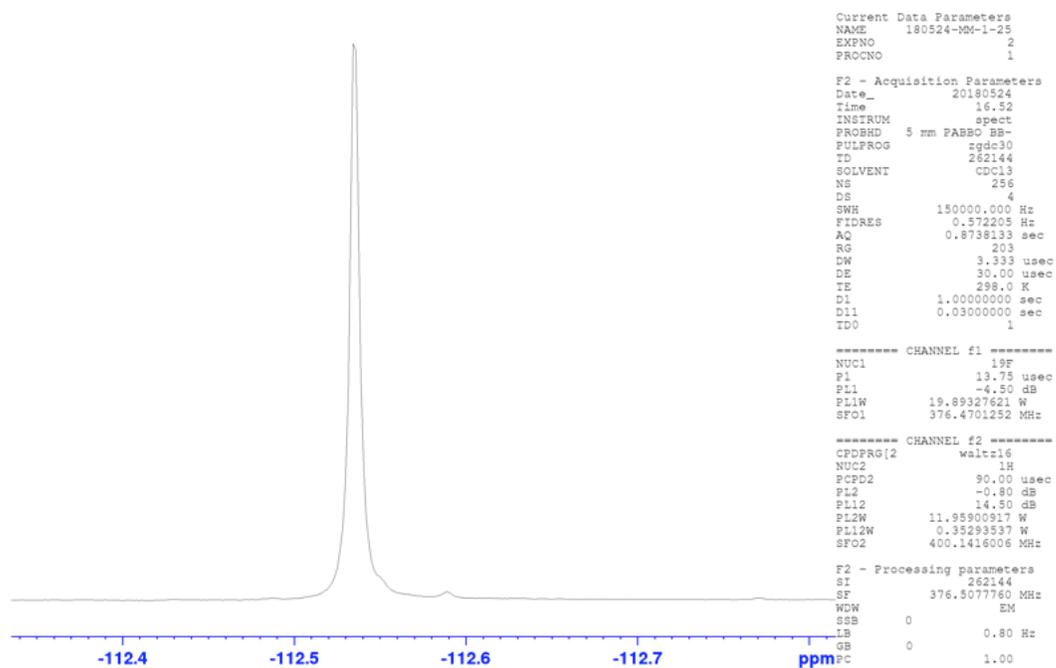


Figure S11: ^{19}F -NMR spectrum of (2) tPDI₂N-benzylF in CDCl₃.

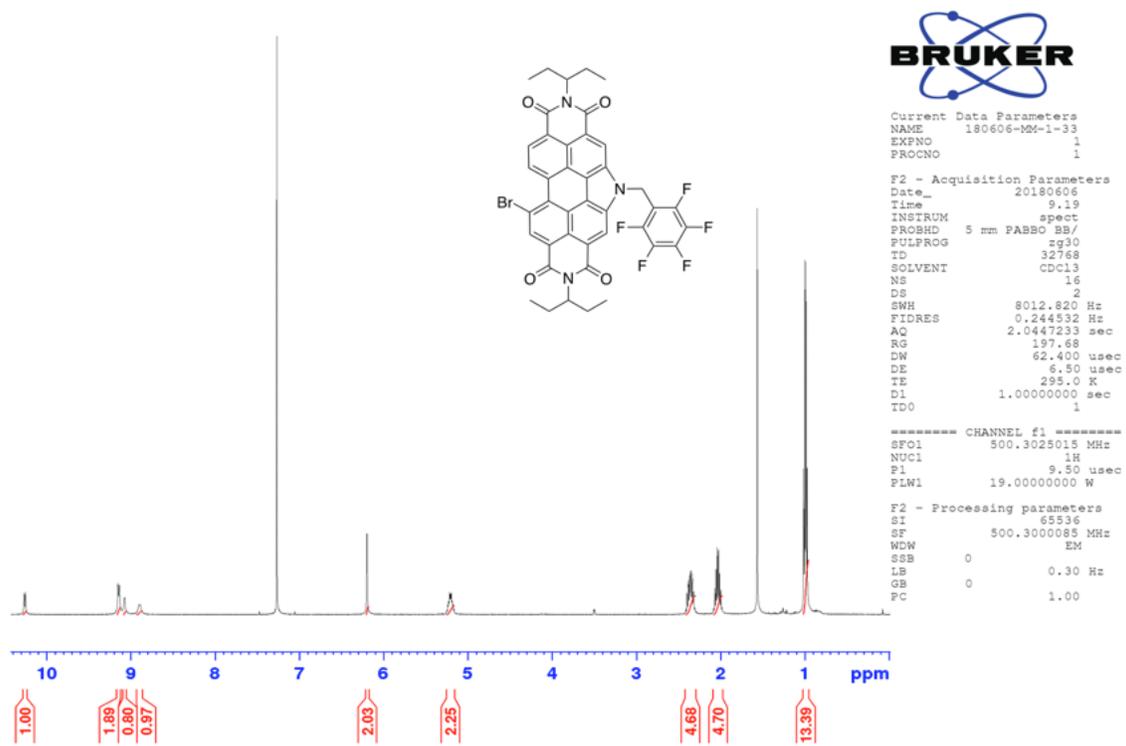


Figure S12: $^1\text{H-NMR}$ spectrum of Br-PDIN-benzylF₅ in CDCl₃.

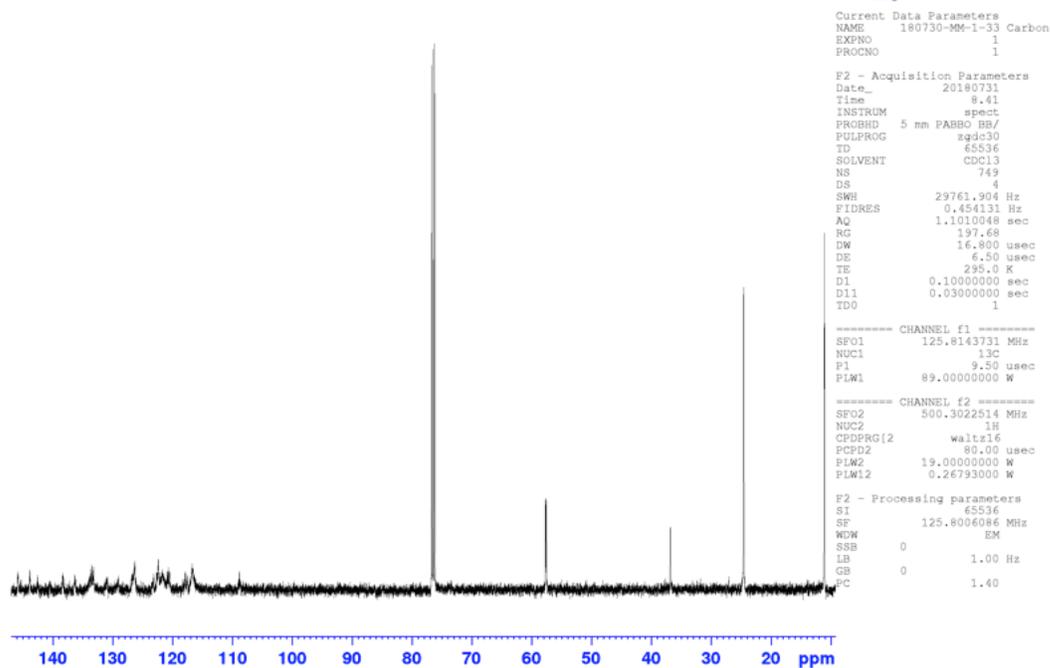


Figure S13: ^{13}C -NMR spectrum of Br-PDIN-benzylF₅ in CDCl₃.

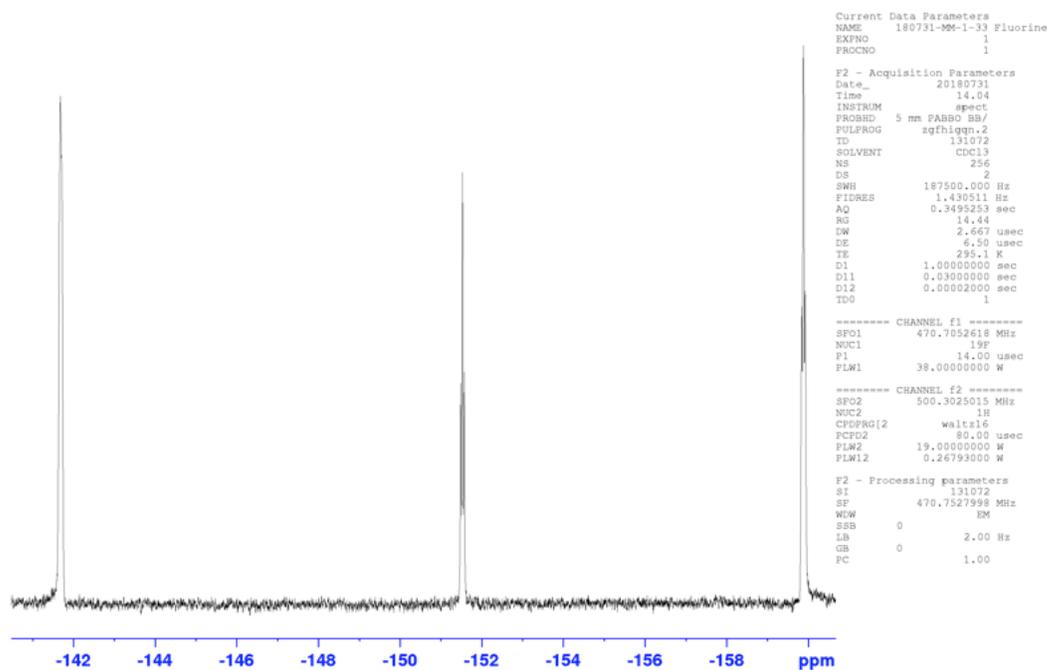


Figure S14: ^{19}F -NMR spectrum of Br-PDIN-benzylF₅ in CDCl₃.

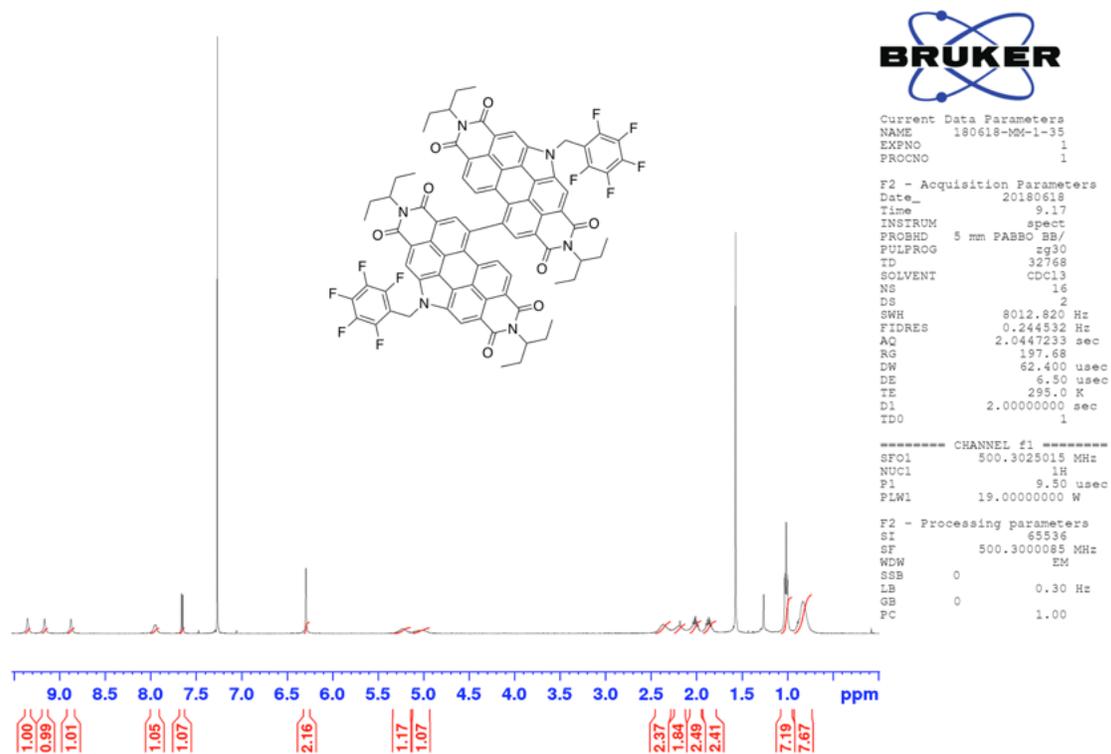


Figure S15: $^1\text{H-NMR}$ spectrum of (3) tPDI₂N-benzylF₅ in CDCl₃.

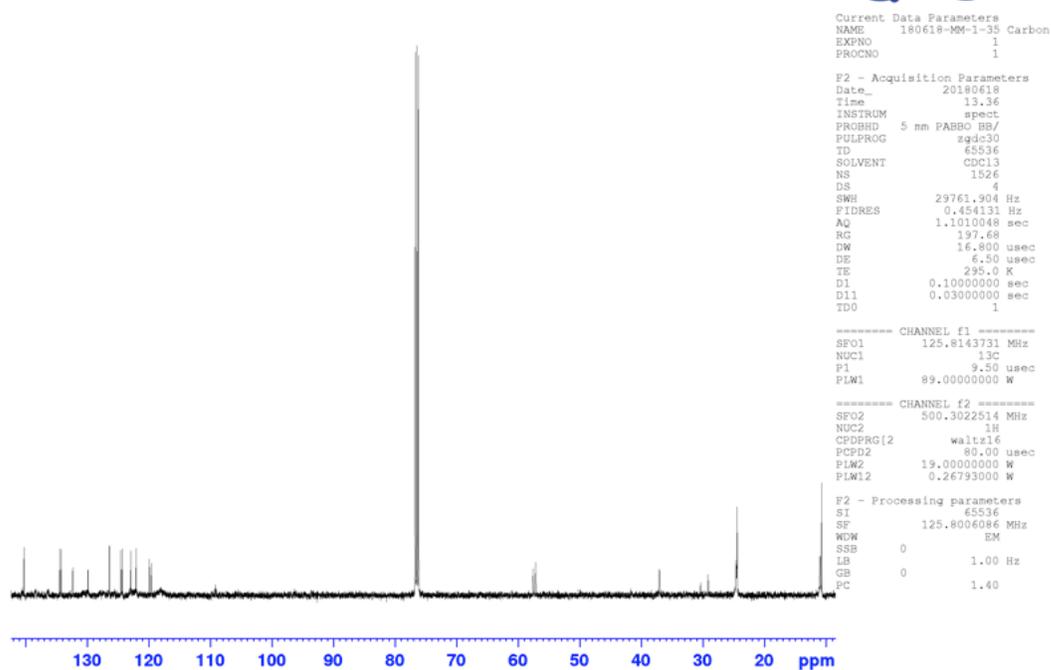


Figure S16: ^{13}C -NMR spectrum of **(3)** tPDI₂N-benzylF₅ in CDCl₃.

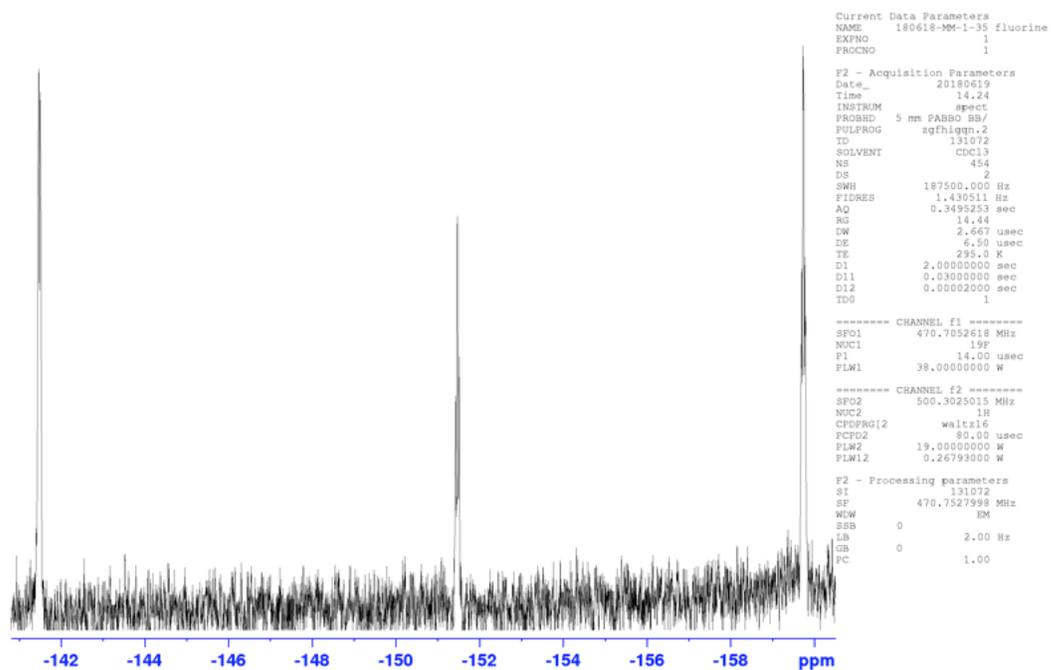


Figure S17: ^{19}F -NMR spectrum of **(3)** tPDI₂N-benzylF₅ in CDCl₃.

4. Mass Spectrometry:

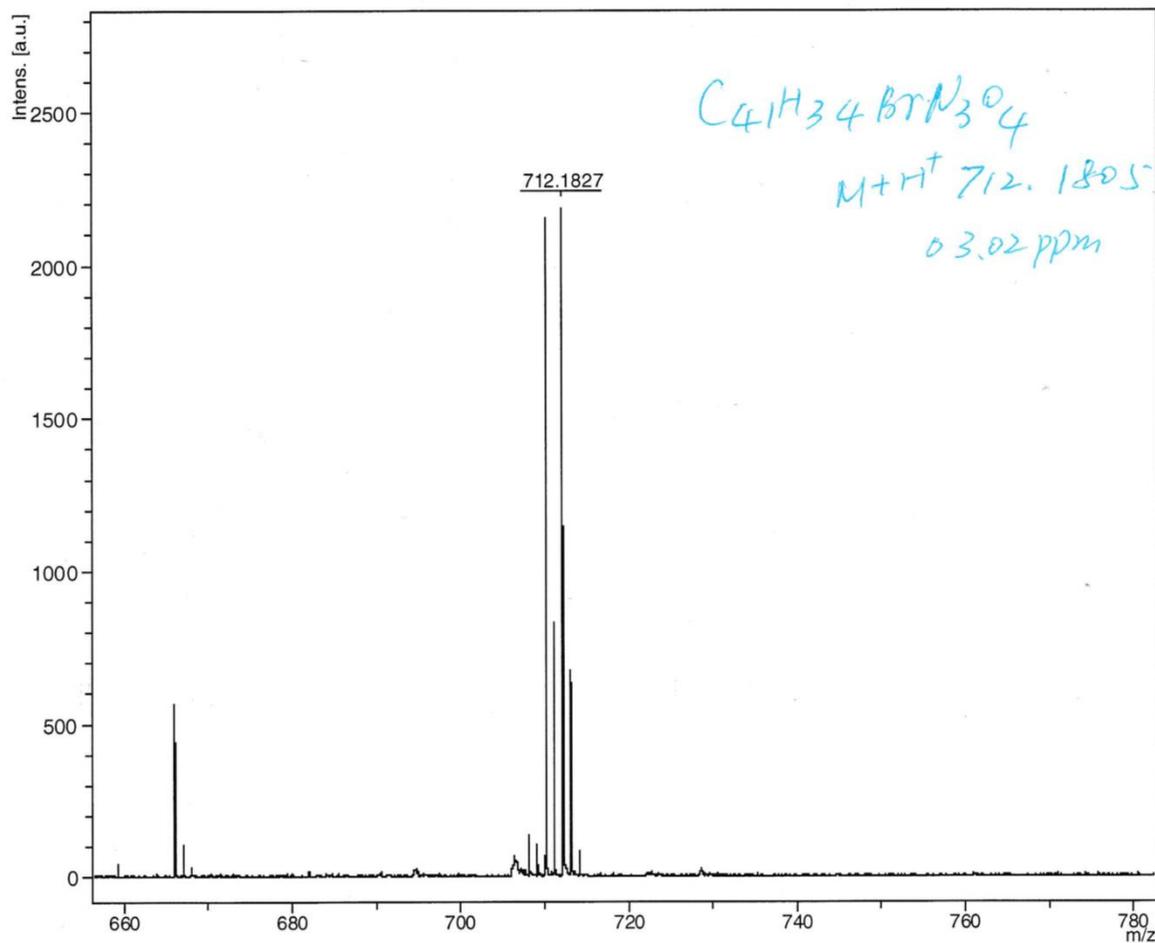


Figure S18: Mass spectrum of Br-PDIN-benzyl.

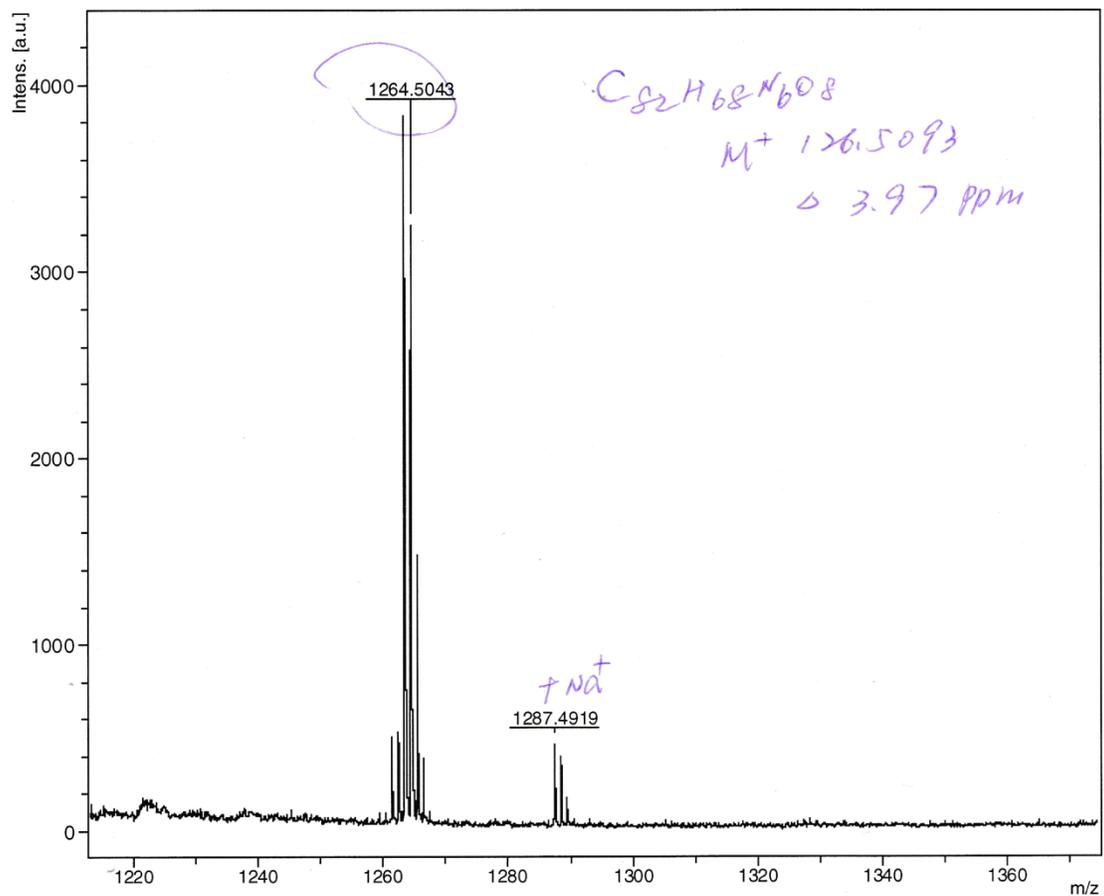


Figure S19: Mass spectrum of (1) tPDI₂N-benzyl.

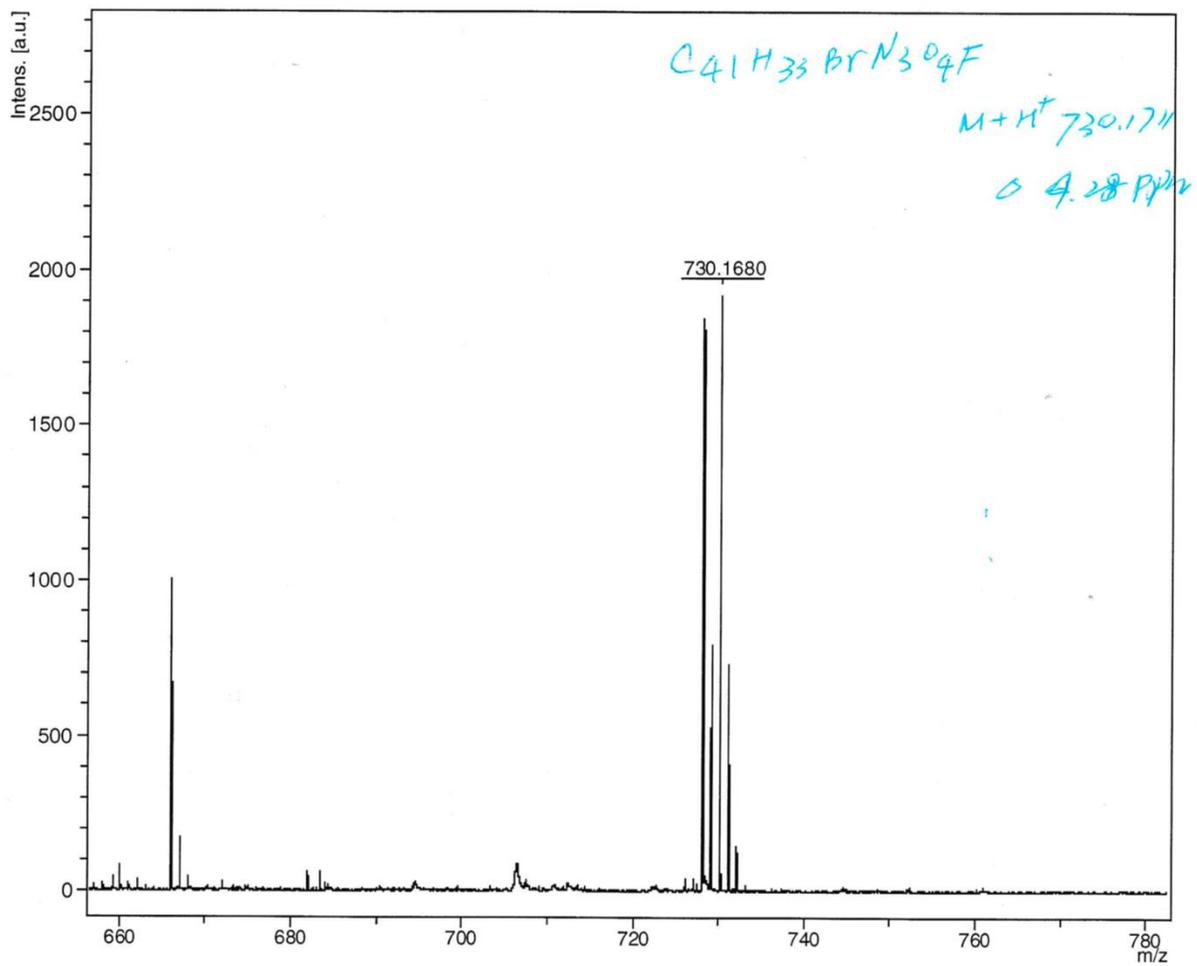


Figure S20: Mass spectrum of Br-PDIN-benzylF.

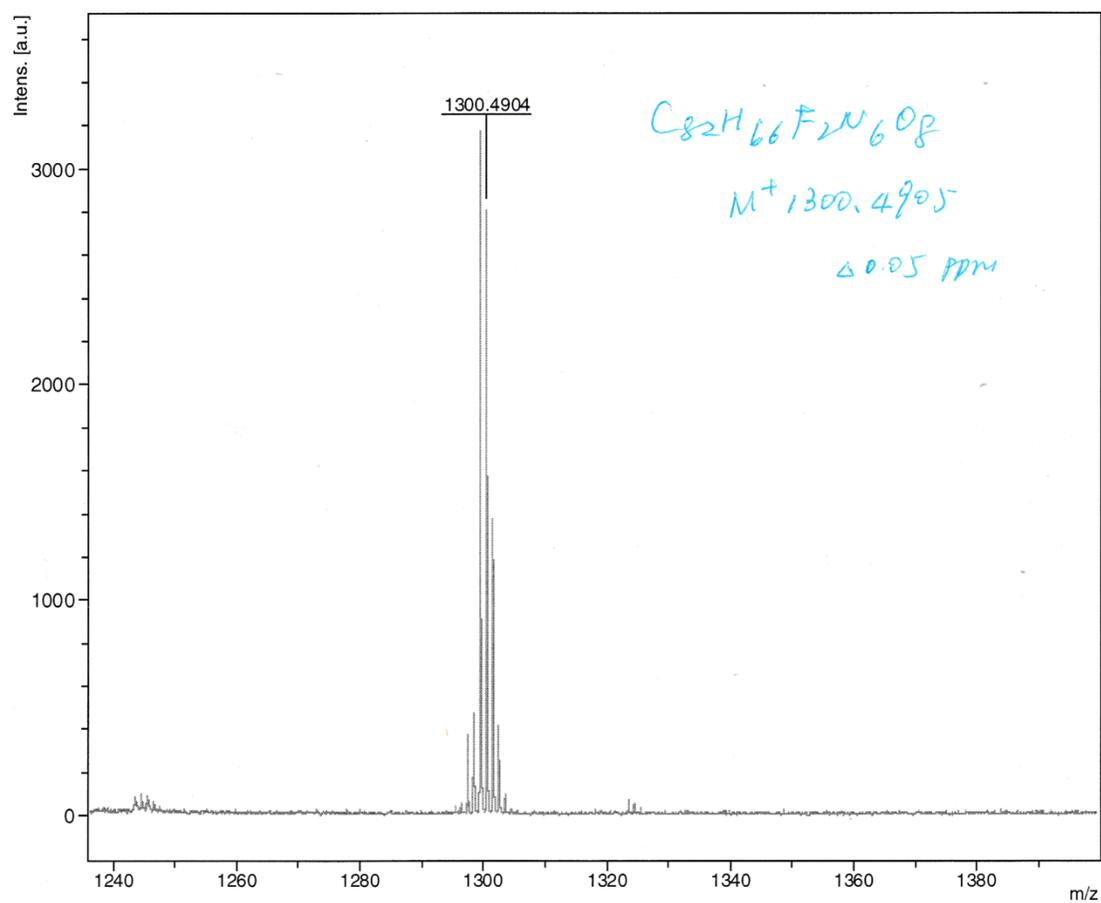


Figure S21: Mass spectrum (2) tPDI₂N-benzylF.

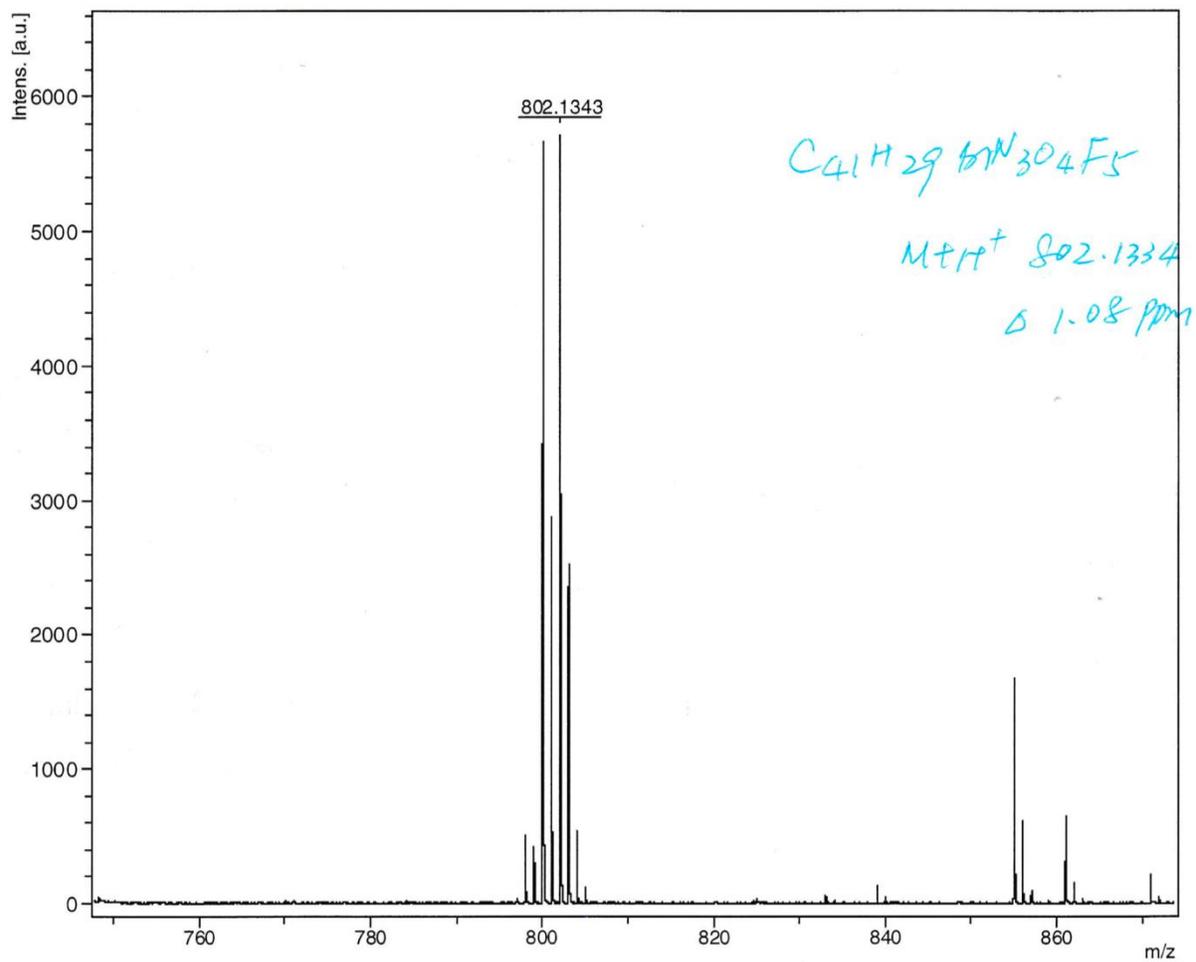


Figure S22: Mass spectrum of Br-PDIN-benzylF₅.

D:\Data\2018\062018\GW\180614MM2.I6.HCCA\0_I6\2

Comment 1 MARK/MM1-35/1442/HCCA

Comment 2

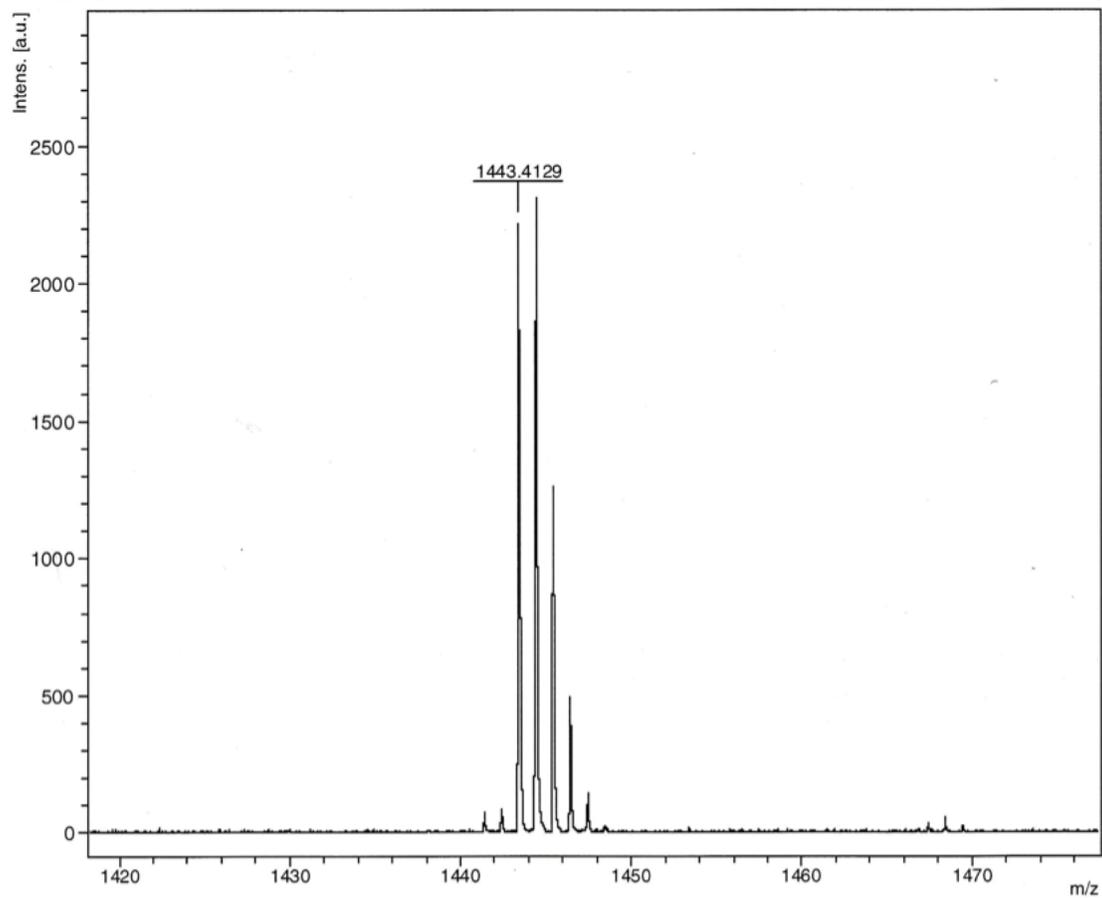


Figure S23: Mass spectrum of (3) tPDI₂N-benzylF₅.

5. Elemental Analysis:

University of Calgary			
Department of Chemistry		EA	Date: 9/5/2018
Name:	TOM	Group:	GW
Sample:	MM1-19-1	Weight (mg):	1.583
%C (Actual):	76.28	%C (Theoretical):	77.83
%H (Actual):	5.26	%H (Theoretical):	5.42
%N (Actual):	6.50	%N (Theoretical):	6.64

Figure S24. Elemental analysis sheet for compound **1** tPDI₂N-benzyl

University of Calgary			
Department of Chemistry		EA	Date: 6/13/2018
Name:	MARK	Group:	GW
Sample:	MM1-25-1	Weight (mg):	1.032
%C (Actual):	74.94	%C (Theoretical):	75.68
%H (Actual):	5.11	%H (Theoretical):	5.11
%N (Actual):	6.27	%N (Theoretical):	6.46

Figure S25. Elemental analysis sheet for compound **2** tPDI₂N-benzylF

University of Calgary			
Department of Chemistry		EA	Date: 6/13/2018
Name:	MARK	Group:	GW
Sample:	MM1-35-1	Weight (mg):	1.078
%C (Actual):	68.04	%C (Theoretical):	68.14
%H (Actual):	4.17	%H (Theoretical):	4.04
%N (Actual):	5.69	%N (Theoretical):	5.81

Figure S26. Elemental analysis sheet for compound **3** tPDI₂N-benzylF₅

6. Thermal Data:

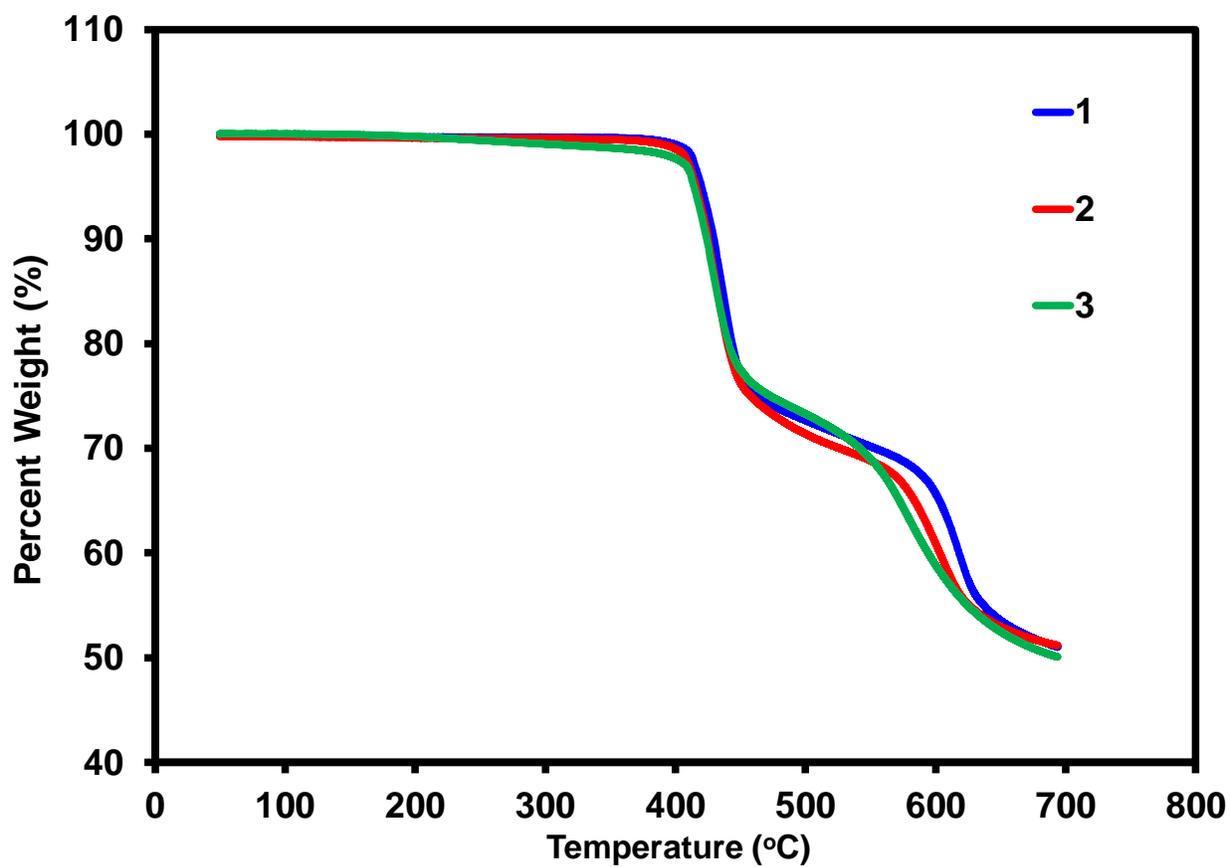


Figure S27: Thermalgravimetric analysis (TGA) plot of PDI materials 1-3.

7. Electrochemical Data:

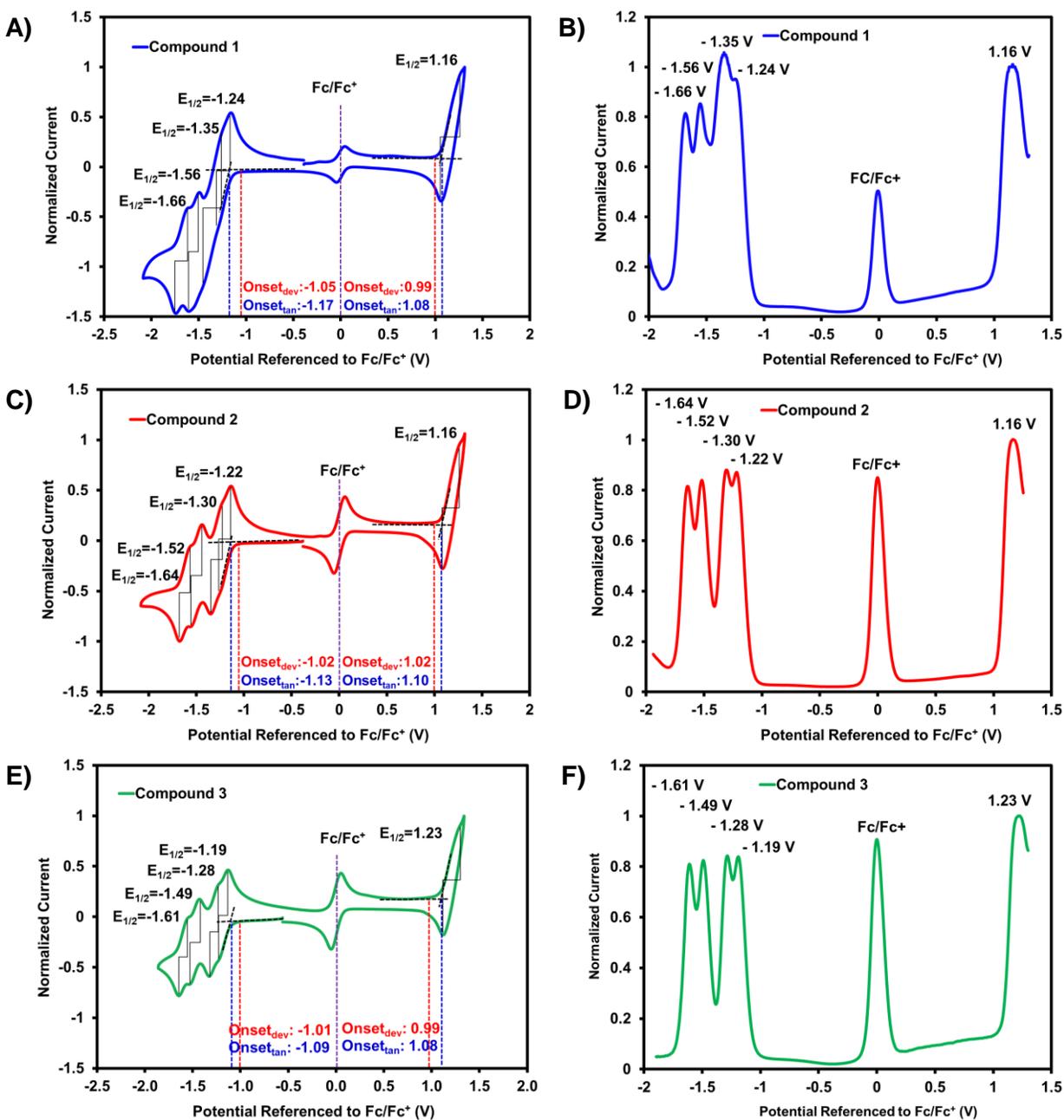


Figure S28. Electrochemical data for PDI materials **1-3**. Cyclic voltammetry traces for (A) **1**, (C) **2**, and (E) **3**. Differential pulse voltammetry traces for (B) **1**, (D) **2**, and (F) **3**. All samples run at 100 mV/s in CH_2Cl_2 solution.

8. Optical Absorption Data:

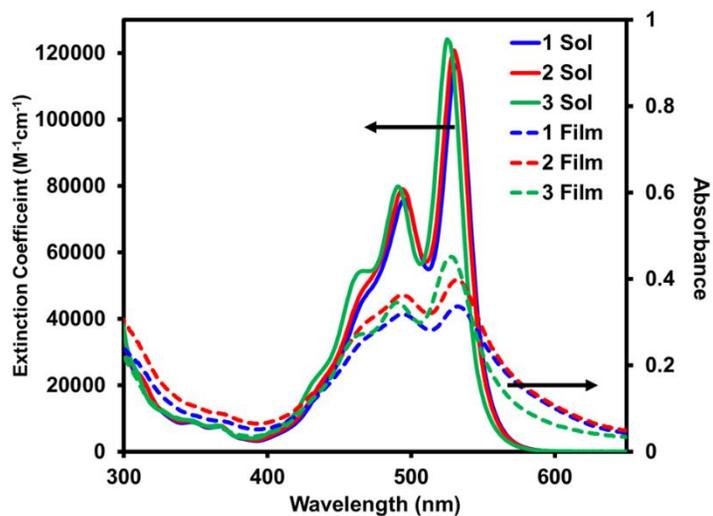


Figure S29. Comparison of solution and film optical absorption spectra of PDI materials **1-3**. Solution spectra recorded in CHCl_3 . Films were cast from 10 mg/mL CHCl_3 solutions.

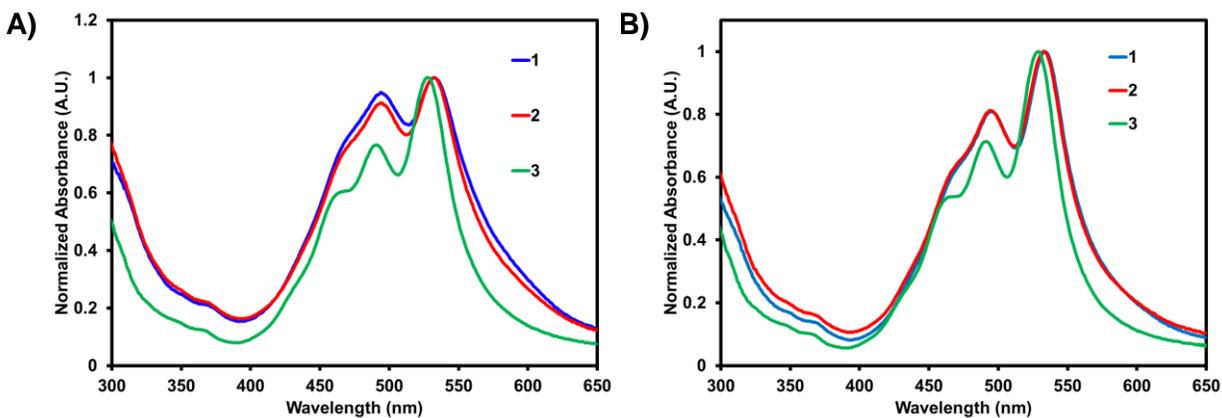


Figure S30. Normalized optical absorption spectra of PDI materials **1-3** in (A) as spun-cast films and (B) after thermal annealing at 180 °C for 10 minutes. Films were cast from 10 mg/mL CHCl_3 solutions.

9. Computational Analysis

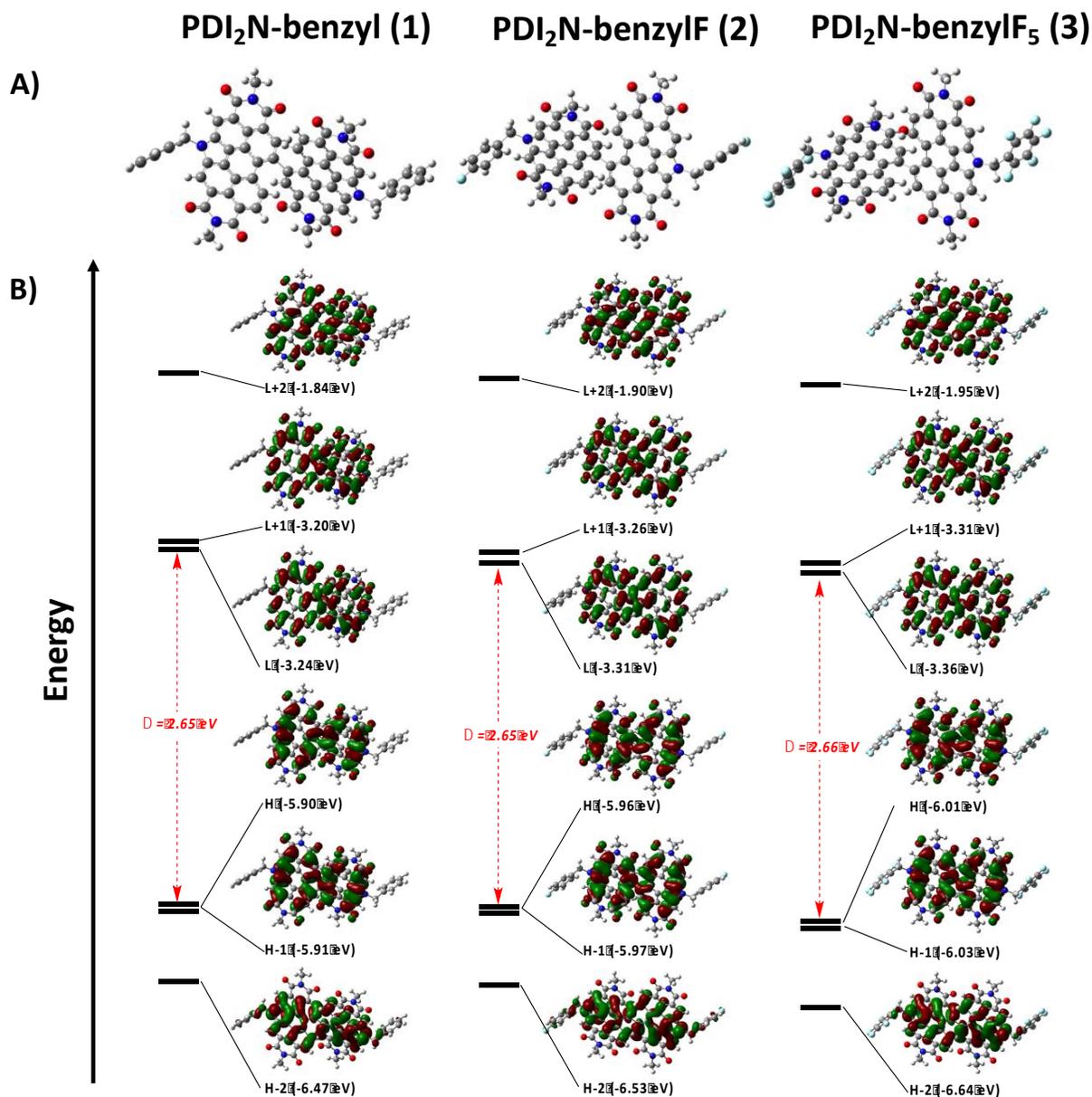


Figure S31: A) Optimized geometry for compounds **1**, **2**, and **3**. B) Calculated electronic energy levels and energy gaps where H = HOMO and L = LUMO. Calculations were done on Gaussian09,² input files and results were visualized using GausView05.³ All alkyl chains were replaced with a methyl group to reduce computational time. The B3LYP⁴⁻⁶ level of theory with 6-31G(d,p)⁷⁻¹² basis set were used for the calculations.

10. Thermal Annealing Study

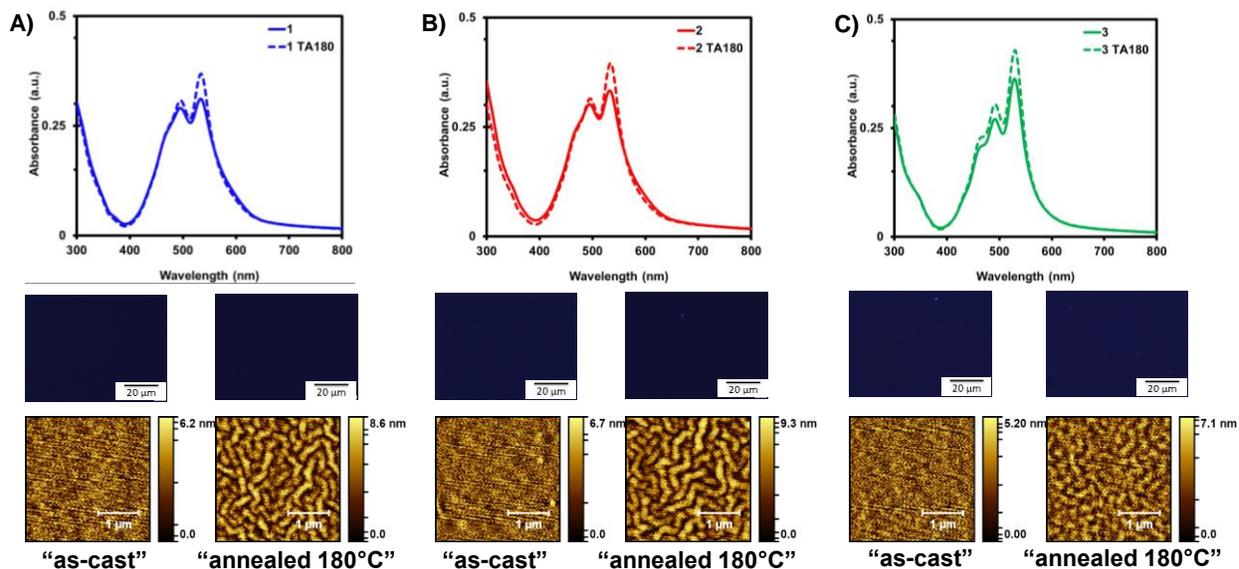


Figure S32. Comparison of films measured 'as-cast' and thermally annealed at 180 °C (TA180) for PDI materials (A) **1**, tPDI₂N-benzyl, (B) **2**, tPDI₂N-benzylF, and (C) **3**, tPDI₂N-benzylF₅. TOP = optical absorption spectra, MIDDLE = polarized light microscopy images, BOTTOM = atomic force microscopy height images. All films were spun-cast (1500 rpm) from CHCl₃ solutions at room temperature.

11. Organic Thin Film Transistors:

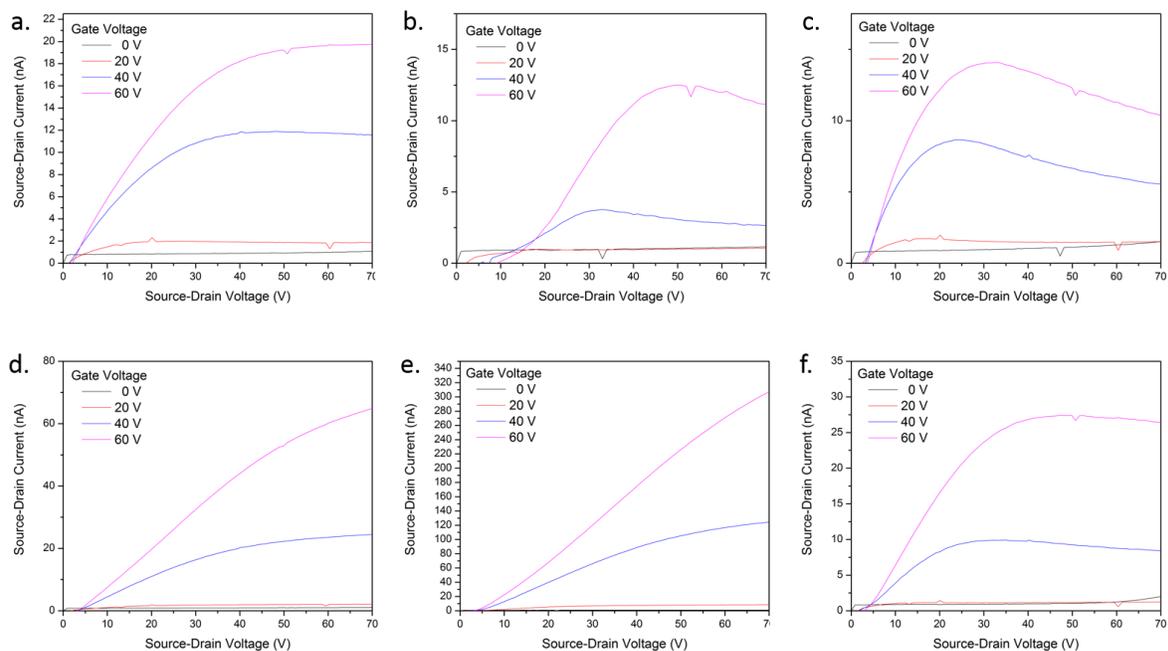


Figure S33: Typical output curves for BGBC OTFTs of **1** (a, d) **2** (b, e) and **3** (c, f) without annealing (a, b, c) and with annealing at 180 °C for 10 minutes (d, e, f).

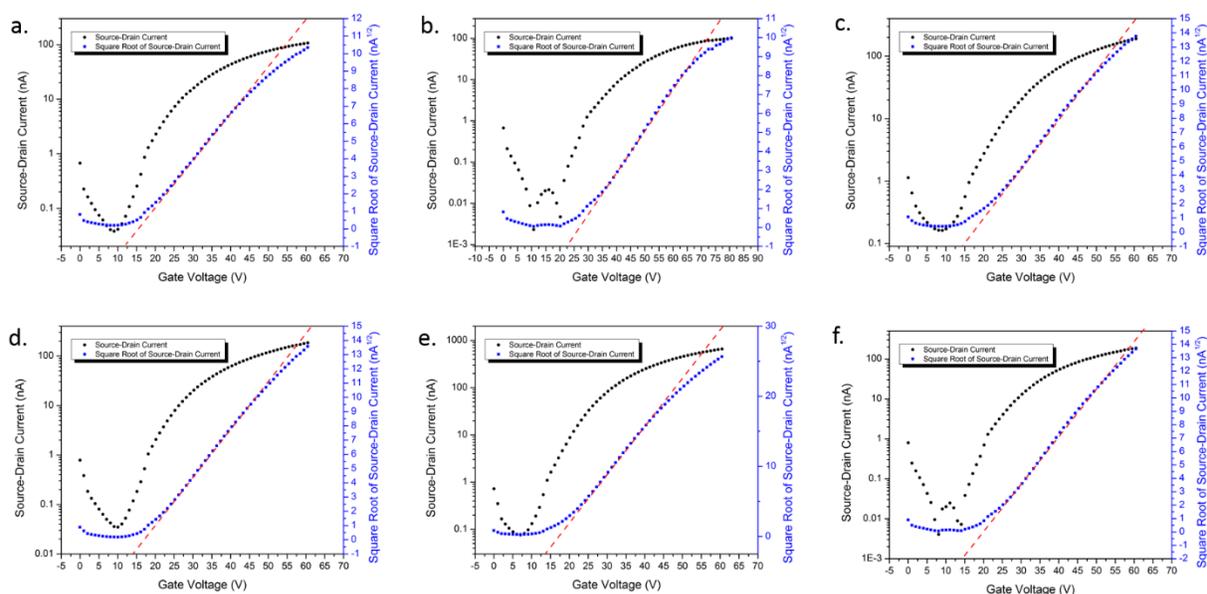


Figure S34: Typical transfer curves with $V_{DS} = 70$ V for BGBC OTFTs of **1** (a, d) **2** (b, e) and **3** (c, f) without annealing (a, b, c) and with annealing at 180 °C for 10 minutes (d, e, f).

12. Organic Solar Cells:

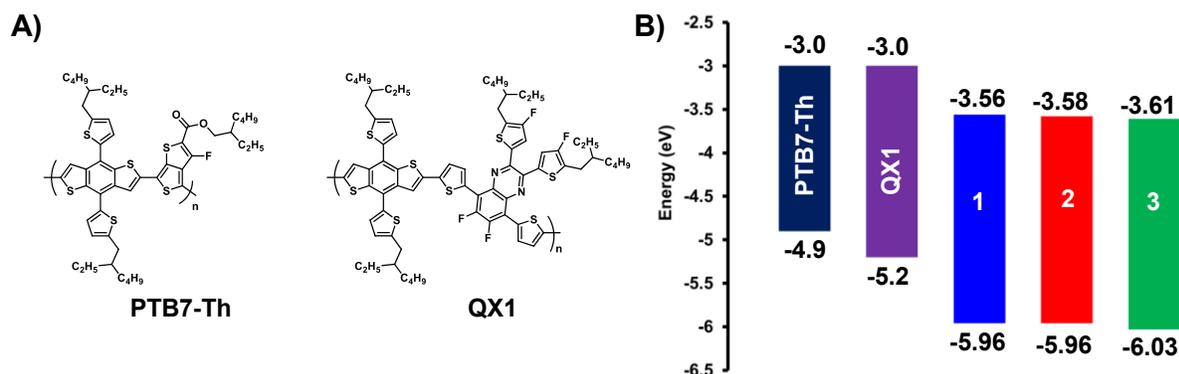


Figure S35. (A) Chemical structures of the donor polymers PTB7-Th and QX1 (TTFQ_x-T1). (B) Electronic energy levels of donor polymers and PDI materials. Donor polymer HOMO/LUMO energy levels determined from the onsets of oxidation and reduction of the solution cyclic voltammetry measurements, respectively, in our labs. PDI materials HOMO/LUMO energy levels determined from the $E_{1/2}$ value of the first oxidation and reduction events. A conversion value of 4.8 was used (see Materials and Methods section).

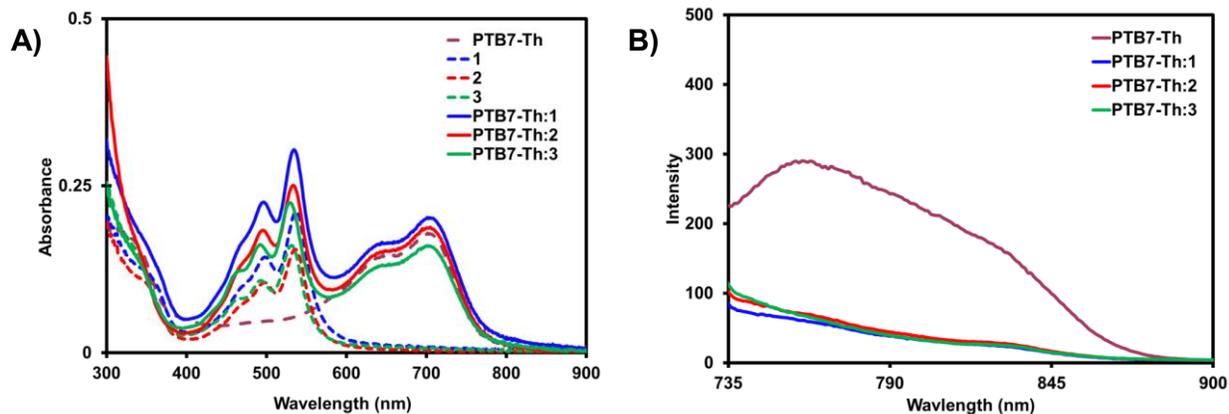


Figure S36. (A) Film optical absorption spectra of donor polymer PTB7-Th, PDI materials **1-3**, and BHJ blends. (B) Film photoluminescent spectra of donor polymer PTB7-Th and BHJ blends. Neat films spun-cast from 5 mg/mL C_6H_5Cl solutions. BHJ blend films cast from 1:1 (polymer:PDI) 10 mg/mL total solids concentration C_6H_5Cl solutions.

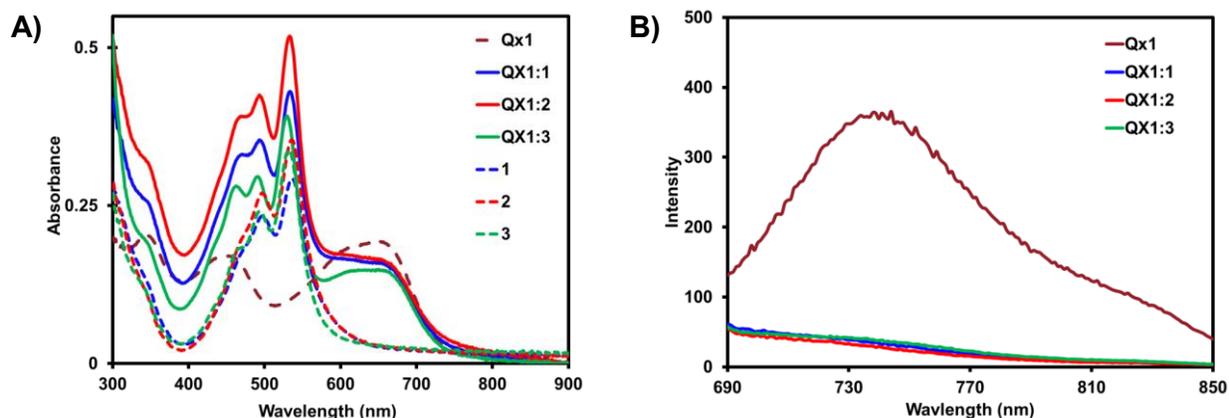


Figure S37. (A) Film optical absorption spectra of donor polymer QX1, PDI materials **1-3**, and BHJ blends. (B) Film photoluminescent spectra of donor polymer QX1 and BHJ blends. Neat films spun-cast from 5 mg/mL 2Me-THF solutions. BHJ blend films cast from 1:1 (polymer:PDI) 10 mg/mL total solids concentration 2Me-THF solutions.

Table S1. OSC data of the PTB7-Th: **PDI** material **1-3** blends (1:1) cast from chlorobenzene. Best results are highlighted in bold. Averages are in italics-blue.

blend	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
PTB7-Th:1	0.93	10.83	48.87	4.92
	0.91	10.38	46.71	4.43
	0.96	11.65	51.10	5.70
	0.93	11.03	50.55	5.19
	0.95	10.85	51.38	5.31
	0.94	10.95	50.95	5.26
	0.93	9.10	50.99	4.31
	0.95	9.87	51.25	4.81
	0.95	9.86	51.23	4.80
	0.93	10.13	48.60	4.60
	0.94	9.72	48.45	4.43
	0.96	9.78	52.57	4.92
	<i>0.94</i>	<i>10.35</i>	<i>50.22</i>	<i>4.89</i>
PTB7-Th:2	0.90	11.02	49.25	4.89
	0.89	8.45	44.32	3.33
	0.89	8.77	51.70	4.04
	0.90	9.10	49.29	4.02
	0.84	9.12	39.25	3.00
	0.91	9.88	50.50	4.52
	0.90	9.89	50.28	4.47
	0.91	10.01	50.58	4.61
	0.91	10.05	49.48	4.50
	0.89	9.97	46.27	4.09
	0.90	8.91	51.67	4.16
	0.90	9.27	51.69	4.34
	<i>0.89</i>	<i>9.54</i>	<i>48.69</i>	<i>4.17</i>
PTB7-Th:3	0.87	9.86	45.80	3.92
	0.87	9.89	45.22	3.90
	0.89	10.18	46.67	4.21
	0.82	10.04	37.41	3.08
	0.88	9.14	47.42	3.82
	0.86	9.06	45.58	3.57
	0.88	9.04	49.02	3.88
	0.88	9.50	47.43	3.95
	0.89	8.94	48.24	3.84
	0.88	9.03	47.06	3.74
	0.89	9.36	48.41	4.03
	0.88	9.33	48.50	3.99
	0.89	9.10	50.29	4.09
	0.89	9.05	50.20	4.04
	0.89	8.79	49.96	3.92
0.88	8.70	49.48	3.80	
<i>0.88</i>	<i>9.31</i>	<i>47.29</i>	<i>3.86</i>	

Table S1. OSC data of the QX1: **PDI** material **1-3** blends (4:6) cast from 2Me-THF. Best results are highlighted in bold. Averages are in italics-blue.

blend	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
QX1:1	0.99	13.35	40.35	5.34
	0.98	13.57	40.16	5.34
	0.99	14.09	41.57	5.82
	0.99	14.19	40.99	5.76
	<i>0.99</i>	<i>13.80</i>	<i>40.77</i>	<i>5.56</i>
QX1:2	0.95	14.37	38.99	5.33
	0.96	14.86	40.43	5.77
	0.96	15.12	40.05	5.82
	0.96	14.40	39.33	5.42
	0.96	14.46	40.04	5.53
	<i>0.96</i>	<i>14.64</i>	<i>39.77</i>	<i>5.57</i>
QX1:3	0.96	14.35	40.05	5.50
	0.95	13.35	39.47	5.02
	0.95	13.39	39.85	5.09
	0.95	14.33	39.96	5.46
	<i>0.95</i>	<i>13.86</i>	<i>39.83</i>	<i>5.27</i>

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