SUPPORTING INFORMATION

N-Annulated Perylene Diimide Dimers: Acetylene Linkers as a Strategy for Controlling Structural Conformation and The Impact on Physical, Electronic, Optical and Photovoltaic Properties

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General Methods:

General synthetic details: Reactions were carried out on a bench top or under an atmosphere of dry, O_2-free N_2 where indicated. For reactions requiring heat, the conventional method involved submerging reaction vial in a LabArmor® bead bath and heating on a hot plate at the desired temperature.

Materials: All materials and solvents were purchased from Sigma-Aldrich unless indicated otherwise. Homogeneous catalysts $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ were purchased from Strem. Heterogeneous catalyst Silia*Cat*® DPP-Pd and heterogeneous Pd scavenger *SiliaMetS*® DMT were purchased from SiliCycle. Polymers PTB7 and PTB7-Th were purchased from One-Material and used as received.

Nuclear Magnetic Resonance (NMR): Reported ^1H and ^{13}C NMR spectra were acquired on either Bruker Ascend 500 mHz, Avance 400 mHZ or DRX 400 mHz spectrometers all at 300 K. For synthetic optimization reactions a Nanalysis Corp NMReady™ 60e 60 mHz spectrometer was used for aliquot NMR samples to confirm the presence of the desired products and assess the extent of reaction. Chemical shifts are reported in parts per million (ppm) and are referenced to the external standard $SiMe_4$. All experiments were performed in $CDCl_3$ or $C_2D_2Cl_4$. Multiplicities are reported as: singlet (s), doublet (d), triplet (t), doublet of doublets (dd), and multiplet (m). We note that compounds **4** and **5** exhibited sharpened ^1H NMR spectra in $C_2D_2Cl_4$ as compared to $CDCl_3$, thus ^1H NMR spectra in the main paper were recorded in $C_2D_2Cl_4$. No significant changes in the chemicals shifts were observed.

Low-Resolution Mass Spectrometry (LRMS): Low-resolution mass spectrometry measurements were performed courtesy of Wade White in the Chemical Instrumentation Facility at the University of Calgary. All samples were run on an Agilent 6520 Q-TOF through direct infusion experiments with an Agilent 1200 series HPLC without a column. The flow rate was 0.2 mL/minute using methanol as the eluting solvent. The source conditions were a gas temperature of 300 °C with a flow of 10 L/min, a vaporizer temperature of 350 °C and a nebulizer pressure of 12 psi.

Elemental Analysis (CHN): Elemental analysis was performed courtesy of Jian Jun (Johnson) Li in the Chemical Instrumentation Facility at the University of Calgary. All samples were run in duplicate on a Perkin Elmer 2400 Series II CHN Analyzer.

Cyclic Voltammetry (CV): All electrochemical measurements were performed using a CH Instruments potentiostat in a standard three-electrode configuration equipped with a silver wire pseudo-reference, platinum wire counter electrode and glassy carbon working electrode. The cyclic voltammetry experiments were performed in an anhydrous solution of dichloromethane (CH_2Cl_2) with ~ 0.1 M tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) supporting electrolyte. Samples were scanned at a rate of 100 mV/s following a dry N_2 purge to deoxygenate the solution. Solution CV measurements were carried out with a sample concentration of ~ 0.5 mg/mL in CH_2Cl_2. Estimations of the energy levels were obtained by correlating the onset (E_{ox} Fc/Fc+, E_{red} Fc/Fc+) to the normal hydrogen electrode (NHE), assuming a IP of 4.80 eV for Fc/Fc+.

$E(IP) = (E_{ox}+4.80)$, $E(EA) = (E_{red}+4.80)$

UV-Visible Spectroscopy (UV/vis): All absorption measurements were recorded using an Agilent Technologies Cary 60 UV-vis spectrometer at room temperature. All solution UV/vis experiments were run in chloroform ($CHCl_3$) using 2 mm quartz cuvettes and diluted 1 % wt/v solutions. Thin-films were prepared by spin-coating 1 % wt/v solutions from $CHCl_3$ onto Corning glass micros slides. 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.

Melting Point Determination: The melting or decomposition points were determined using a Stuart SMP40 apparatus operating from 50 to 400 °C with a ramp rate of 20 °C per minute.

UPS/IPES: For photoelectron spectroscopy (PES), thin films were prepared using 2 mg/mL solutions of each compound in chlorobenzene spun onto ITO coated glass substrates at 5000 rpm. For UPS, the analysis chamber was equipped with a hemispherical energy analyzer (Specs Phoibos 150). The UPS measurements were carried out using a He I (hν = 21.22 eV) source. A sample bias of −3 V was used to overcome the contact potential difference during measurement of the onset of photoemission (resulting UPS data are corrected for this bias). IPES measurements were performed in the isochromat mode using a homemade spectrometer located in the PES analysis chamber, with a resolution of approximately 0.6 eV as determined by the width of the Fermi edge of clean polycrystalline silver. The positions of the Fermi edge were used to align the UPS and IPES energy scales. All PES measurements were performed at a base pressure of 10^{-10} mbar.

Thermogravimetric analysis (TGA): TGA was carried out using a simultaneous thermogravimetric analysis/differential scanning calorimetry (TGA/DSC) analyzer (SDT Q600, TA Instruments, Inc., New Castle, DE). Approximately 2 mg of dried solid was heated at 10 °C min^{-1}. The nitrogen flow was kept at 100 cm^3 min^{-1} during the experiments. The experiments were performed under ambient pressure. The TGA instrument was calibrated for mass and heat changes using sapphire as a reference for heat calibration and zinc as a reference for temperature calibration.

Solar Cell Device Fabrication and Testing:

Chlorobenzene processed devices: Prepatterned ITO coated glass substrates (Thin Film Devices) were ultrasonicated in DI water with detergent, DI water, acetone, and ethanol. Substrates were blown dry with air and underwent 20 minutes of UV-ozone treatment. 100 mg/mL zinc acetate dihydrate in 2-methoxyethanol with 30 µL/mL ethanolamine was spun onto the substrates at 4000 rpm and annealed at 200 °C in air for 1 hr. The resulting zinc oxide coated substrates were transferred to a N_2 filled glovebox for active layer casting. Active layer solutions were cast from 25 mg/mL solutions in chlorobenzene at 1500 rpm with the specified blend ratios. All active layer solutions were filtered through a 0.45 µm PTFE filter prior to casting. Next, 15 nm of MoO_3 was thermally deposited under vacuum (10^{-6} mbar) at a rate of 0.2-0.5 Å/s. Finally, 100 nm of Ag was thermally deposited under vacuum through a shadow mask at a rate of 1 Å/s to make devices with an area of 0.0325 cm^2.

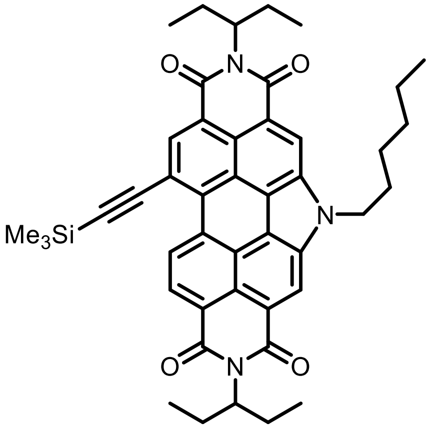
Chloroform processed devices: Devices were fabricated using ITO-coated glass substrates cleaned by sequentially ultrasonicating detergent and de-ionized water, acetone and isopropanol followed by exposure to UV-zone for 30 minutes. ZnO was deposited as a sol-gel precursor solution in air following the method of Sun et al (Y. Sun, J. H. Seo, C. J. Takacs, J. Seifter and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 1679–1683). The room temperature solution was filtered and spin-cast at a speed of 4000 rpm and then annealed at 200 °C in air for 1 hour. Active layer solutions were cast from 10 mg/ml solution in chloroform at 1500rpm with the 40:60 blend ration. All solutions were stirred overnight at room temperature prior to filtration through a PTFE filter. The substrates were then allowed to dry in the glowbox overnight before depositing the top contacts. Top contacts of MoO_3 (10 nm) followed by 100 nm of silver were thermally deposited under vacuum about 4*10-6 torr. The active areas of resulting devices were 0.09 cm^2.

Completed devices were then tested in air using a Newport 92251A-1000 AM 1.5 solar simulator which had been calibrated using a standard silicon solar cell (Newport 91150V) to obtain an irradiance level of 1000 W/m^2.

Solar cell characterization: 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 1000 W/m^2 under a Solar Simulator (Newport 92251A-1000). The standard silicon solar cell (Newport 91150V) was used to calibrate light intensity. EQE was measured in a QEX7 Solar Cell Spectral Response/QE/IPCE Measurement System (PV Measurement, Model QEX7, USA) with an optical lens to focus the light into an area about 0.04 cm^2, smaller than the dot cell (0.09 cm^2). The silicon photodiode was used to calibration of the EQE measurement system in the wavelength range from 300 to 1000 nm. AFM measurements were performed by using a Scanning Probe Microscope-Agilent Technologies 5500 in contact mode. We used probe with contact aluminum coated (PEN-0054-00, NanoInk, Inc). The surface active layers of solar cells were measured by AFM between the top silver contacts

Synthesis:

Synthesis of PDIACTMS (1a):

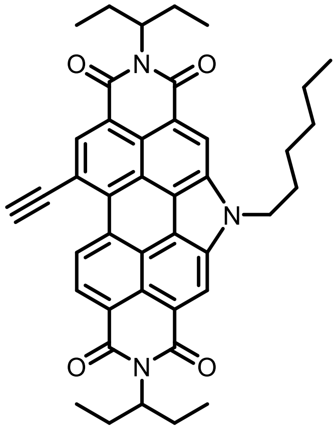


Compound **1a** was synthesized via Sonogashira coupling of **1** with trimethylsilylacetylene using a modified literature procedure.[1] We found that the ensuing deprotection of the acetylene (removal of the TMS protecting group) would prove problematic and form the dimeric species (**5**) in addition to the desired product if there was any residual palladium contamination. Therefore, two methods were employed to ensure minimal palladium contamination. **Method A** utilized a heterogeneous palladium catalyst to install TMS-acetylene group. **Method B** utilized a homogenous catalyst to install the TMS-acetylene group, followed by treatment of the product with a heterogeneous Pd scavenger. We found that both methods were effective at minimizing Pd contamination and enabling a clean deprotection, but Method A resulted in a lower yield of **1a**.

Method A: PDI-Br, **1**, (500 mg, 0.7 mmol), copper iodide (5 mg, 0.02 mmol, 3%), and Siliacat ® DPP-Pd (80 mg, 0.02 mmol Pd, 3%) were added to a 20 mL microwave vial. The mixture was purged with nitrogen for 10 minutes. Diisopropylamine (10 mL), and trimethylsilylacetylene (0.2 mL, 1.4 mmol) were then added. The reaction was heated in a bead bath to 75 °C with stirring for 24h. After cooling to room temperature, the reaction was diluted with 50 mL DCM and filtered through silica. The solvent was removed under reduced pressure. The red product was isolated from methanol. To remove residual impurities silica gel chromatography was used with a hexanes to DCM gradient to give **1a** as a red solid (0.257 g, 51%).

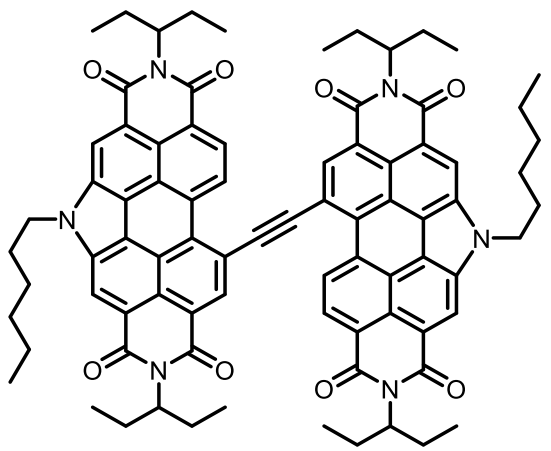
Method B: PDI-Br (1g, 1.4 mmol), CuI (8 mg, 0.04 mmol, 3%), and $Pd(PPh_3)_4$ (45 mg, 0.04 mmol, 3%) were added to a 20 mL microwave vial. The vial was sealed and purged with nitrogen for 10 minutes. To this mixture was added 20 mL of diisopropylamine and TMS-acetylene (0.4 mL, 2.8 mmol). The reaction was stirred and heated to 40 °C for 24h. The reaction was then diluted with 50 mL THF and, using 20 mL more THF, filtered through 1 cm silica. The red solution was concentrated under reduced pressure to give a red solid. The solid was dissolved in 50 mL DCM and 0.5 g SiliaMetS® Dimercaptotriazine (Pd scavenger) was added. This mixture was stirred for 4h at room temperature before filtering over 1 cm Celite to remove the scavenger. To the filtrate was added 10 mL methanol and the solvent was removed under reduced pressure to give **1a** (1g, 1.37 mmol, 98%) as a dark purple powder which was isolated from methanol.

Synthesis of PDIAC (2):



To a 250 ml round bottom flask containing PDIACTMS, **1a** (1.9g, 2.5 mmol) and potassium carbonate was added 100 mL each of chloroform and methanol. The resulting mixture was stirred for 10 minutes before filtering through silica with additional DCM to remove the residual potassium carbonate. The solvent was removed from the red filtrate under reduced pressure. The purple solid was isolated from methanol to give **2**(1.707g, 2.5 mmol, 99%). No further purification was necessary.

Synthesis of PDI$_2$AC (4):



To a 20 mL microwave vial was added PDIAC, **2** (202 mg, 0.311 mmol), PDI-Br (200 mg, 0.28 mmol), Pd(PPh$_3$)$_4$ (16 mg, 0.014 mmol, 5%) and CuI (5 mg 0.028 mmol, 10%). The vial was capped and purged with nitrogen gas for 15 minutes. To the sealed vial was added 10 mL deoxygenated toluene and 1 mL dry diisopropylamine. The reaction mixture was heated to 60 °C for 1 hour, until thin layer chromatography indicated completion of the reaction. The purple solution was diluted with DCM and filtered through a 1 cm thick pad of celite to remove metal catalysts. The solvent was removed from the filtrate under reduced pressure to give **4** as a purple solid which was isolated from acetone (350 mg, 0.31 mmol, 98%). To ensure minimal metal contamination and neutralize any acidic sites, **4** was dissolved in DCM and slurried with Celite® 545 for 30 min before filtering through alumina. Mp > 400°C (**4** did not melt below the limit of our instrument).

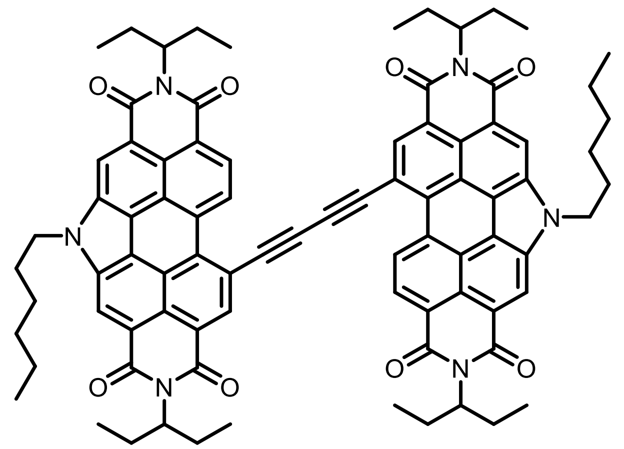
ESI Mass Spec: Calculated 1276.6 Observed: 1277.6

Elemental Analysis:

Calculated: C 77.09%, H 6.31%, N 6.58%.

Observed: C 76.21%, H 6.42%, N 6.31%

Synthesis of PDI$_2$Ac$_2$ (5):



To a 100 ml round bottom flask containing (200 mg, 0.3 mmol), copper iodide (6 mg, 0.03 mmol 10%), potassium carbonate (124 mg, 0.9 mmol) and Pd(PPh$_3$)$_2$Cl$_2$ (35 mg, 0.03 mmol 10%) was added 10 mL chloroform and 10 ml methanol. The solution was stirred, open to air for 3 hours, until thin layer chromatography indicated completion of the reaction. The purple solution was filtered over silica with THF to remove metal catalysts. The solvent was removed from the purple filtrate under reduced pressure to give a **5** (205 mg) as a purple solid. PDI$_2$Ac$_2$ was purified via silica column chromatography using silica pretreated with 3 column volumes of 2% TEA in hexanes and a gradient of hexanes to DCM. (140 mg, 0.11 mmol, 70%) mp: 337-339°C.

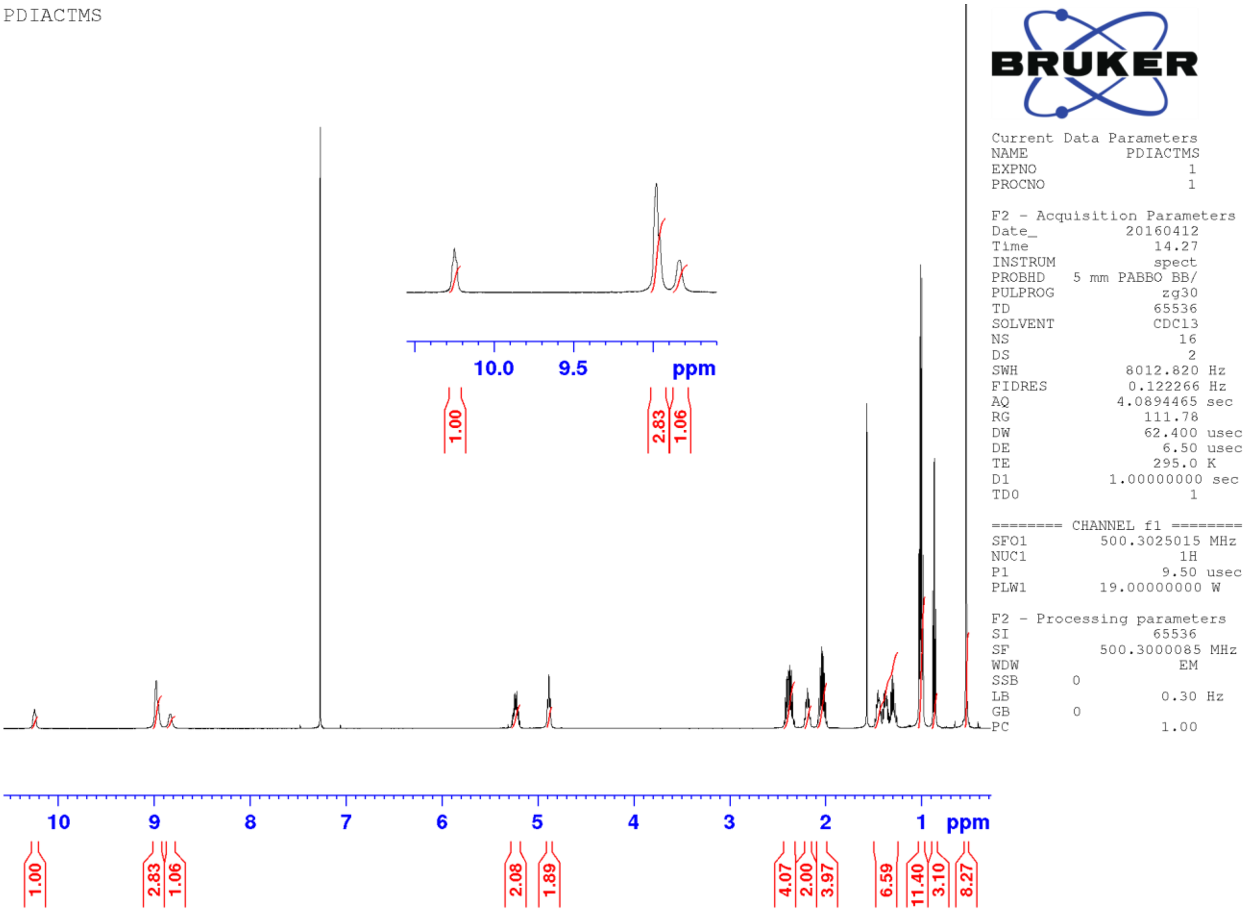
ESI and APCI Mass Spec: Unable to obtain spectrum

Elemental Analysis:

Calculated: C 77.50%, H 6.20%, N 6.46%.

Observed: C 75.86%, H 6.07%, N 6.03%

NMR Spectra:



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PROCNO                   1

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PULPROG               zg30
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NS                      16
DS                       2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                  111.78
DW                  62.400 usec
DE                    6.50 usec
TE                   295.0 K
D1             1.00000000 sec
TD0                      1

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NUC1                    1H
P1                    9.50 usec
PLW1          19.00000000 W

F2 - Processing parameters
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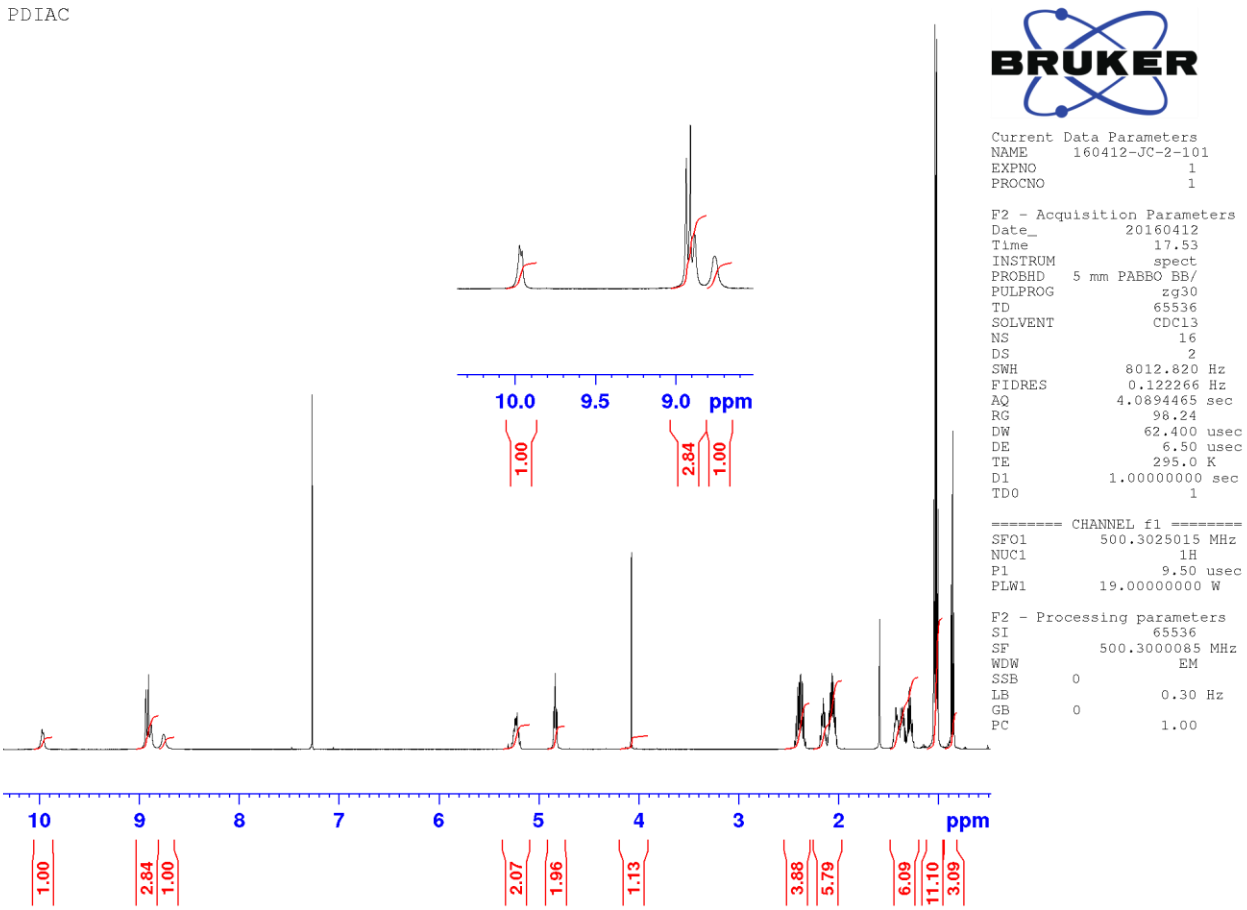
SF            500.3000085 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Figure S1. ^{1}H NMR spectra of **PDIACTMS (1a)**: **^{1}HNMR ($CDCl_3$):** 10.25 (s, 1H); 8.98 (m, 3H); 8.83 (m, 1H); 5.23 (m, 2H); 4.88 (t, $J_{H\text{-}H}$ = 7 Hz); 2.43-2.33 (m, 4H); 2.22-2.15 (m, 2H), 2.09-2.00 (m, 4H); 1.49-1.25 (m, 6H); 1.00 (q, $J_{H\text{-}H}$ = 9 Hz, 12H); 0.87 (t, $J_{H\text{-}H}$ = 9 Hz, 3H); 0.53 (s, 9H).



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PROCNO                  1

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TD                  65536
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NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                  98.24
DW                 62.400 usec
DE                   6.50 usec
TE                  295.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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NUC1                   1H
P1                   9.50 usec
PLW1          19.00000000 W

F2 - Processing parameters
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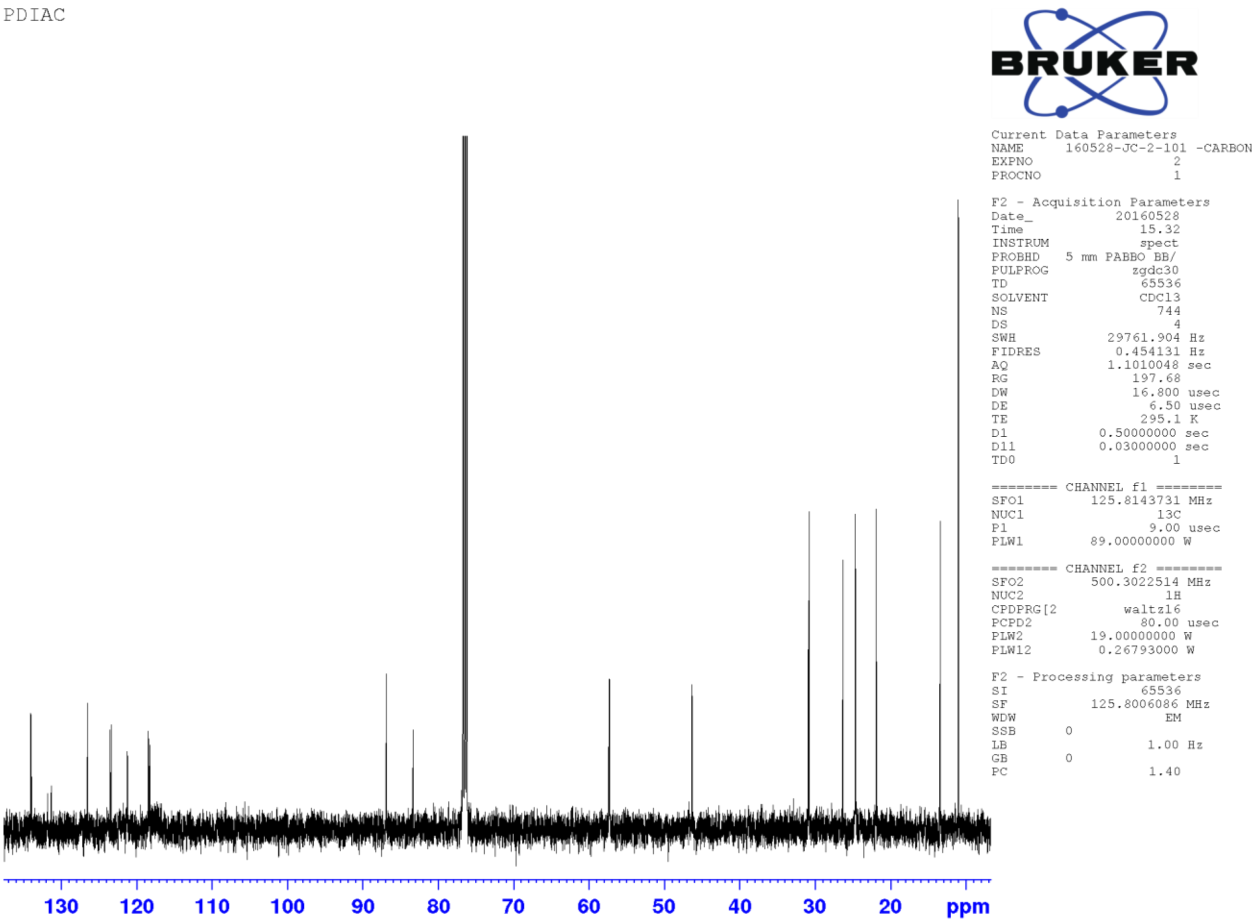
SF            500.3000085 MHz
WDW                    EM
SSB       0
LB                   0.30 Hz
GB        0
PC                   1.00
```

Figure S2. ^{1}H NMR spectra of **PDIAC (2)**: **^{1}HNMR (CDCl$_3$):** 9.97 (m, 1H); 8.95-8.86 (m, 3H); 8.75 (m, 1H); 5.27-5.19 (m, 2H); 4.83 (t, $J_{H\text{-}H}$ = 7 Hz. 2H); 4.08 (s, 1H); 2.44- 2.33 (m, 4H); 2.18-2.02 (m, 6H); 1.46-1.25 (m, 7H); 1.03 (q, $J_{H\text{-}H}$ = 7 Hz, 12H); 0.86 (t, $J_{H\text{-}H}$ = 7 hz, 3H).

APCI Mass Spec: Calculated: 651.31 Observed: 652.3189



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PROCNO                   1

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PULPROG            zgdc30
TD                  65536
SOLVENT             CDCl3
NS                    744
DS                      4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 197.68
DW                 16.800 usec
DE                   6.50 usec
TE                  295.1 K
D1             0.50000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          125.8143731 MHz
NUC1                  13C
P1                   9.00 usec
PLW1          89.00000000 W

======== CHANNEL f2 ========
SFO2          500.3022514 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2          19.00000000 W
PLW12          0.26793000 W

F2 - Processing parameters
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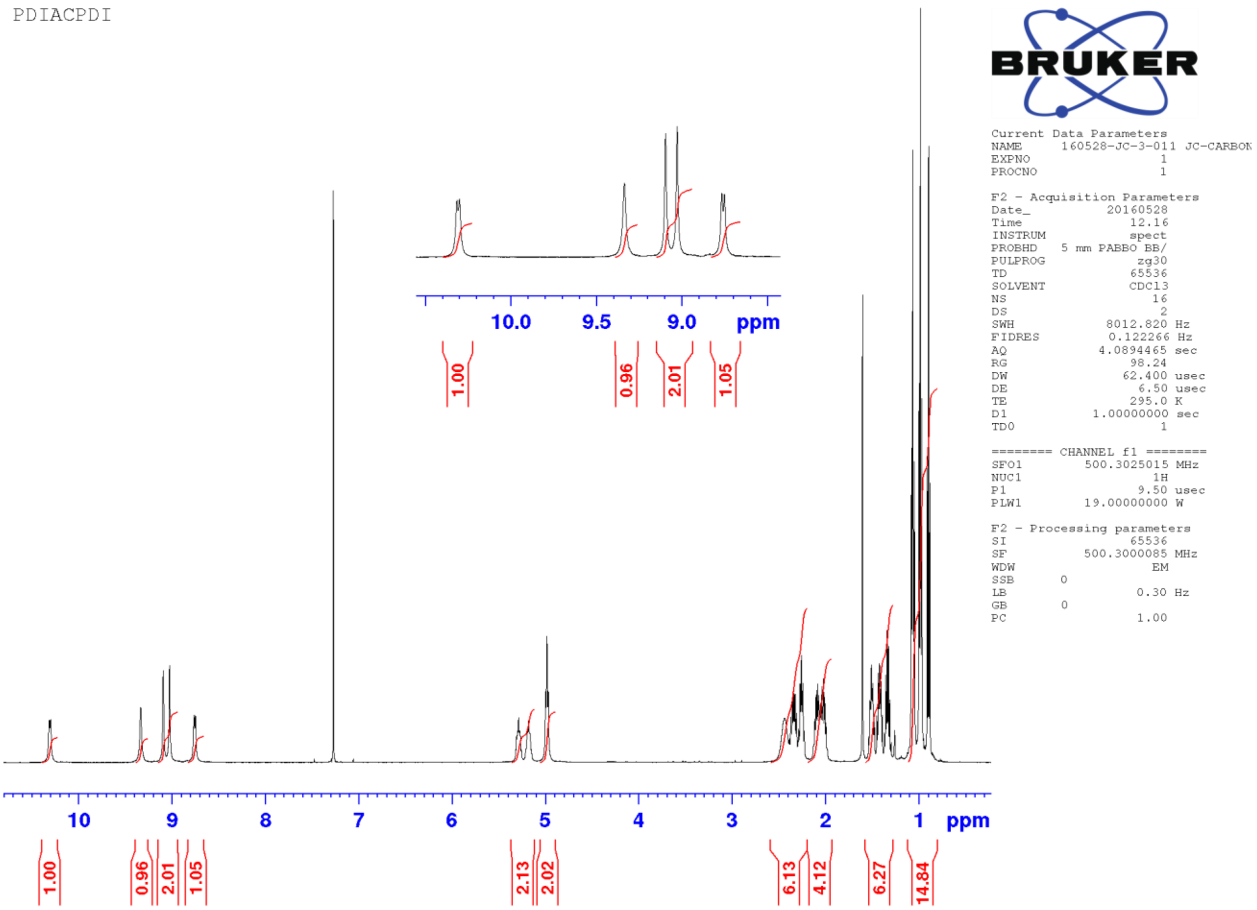
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

Figure S3. ^{13}C NMR spectra of **PDIAC (2)**: **^{13}CNMR (CDCl$_3$):** 134.1, 134.0 131.4, 126.5, 123.5, 123.4, 121.3, 121.2, 118.5, 118.4, 118.3, 86.9, 83.3, 76.7, 76.5, 76.2, 57.3, 57.3, 46.3, 30.9, 30.9, 26.3, 24.7, 24.6, 21.9, 13.4.



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PROCNO                   1

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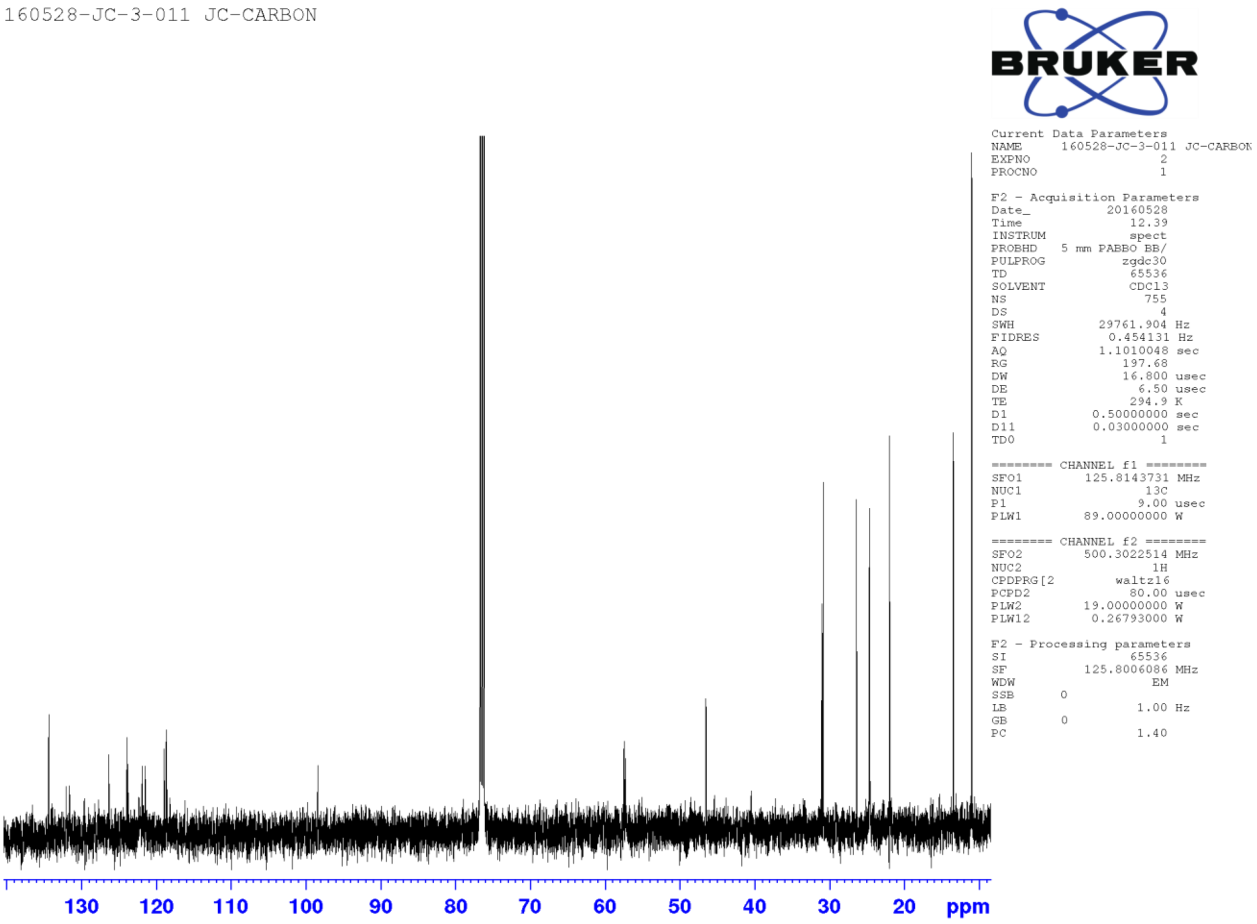
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                  98.24
DW                 62.400 usec
DE                   6.50 usec
TE                  295.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          500.3025015 MHz
NUC1                   1H
P1                   9.50 usec
PLW1          19.00000000 W

F2 - Processing parameters
SI                  65536
SF            500.3000085 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Figure S4. ^{1}H NMR spectra of **PDI$_2$AC (4)**: **^{1}HNMR (CDCl$_3$):** 10.46 (d, J$_{H-H}$ = 9 Hz, 2H); 9.37 (s, 2H); 9.16 (s, 2H); 9.08 (s, 2H); 8.84 (d, J$_{H-H}$ = 9 Hz, 2H); 5.31 (m, 2H); 5.21 (m, 2H); 5.00 (t, J$_{H-H}$ = 9 Hz, 4H); 2.53-2.25 (m, 16H); 1.54-1.33 (m, 12H); 1.10-0.88 (m, 30H).



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EXPNO                    2
PROCNO                   1

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PULPROG            zgdc30
TD                   65536
SOLVENT              CDCl3
NS                     755
DS                       4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                  197.68
DW                  16.800 usec
DE                    6.50 usec
TE                   294.9 K
D1             0.50000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          125.8143731 MHz
NUC1                   13C
P1                    9.00 usec
PLW1           89.00000000 W

======== CHANNEL f2 ========
SFO2          500.3022514 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                80.00 usec
PLW2           19.00000000 W
PLW12           0.26793000 W

F2 - Processing parameters
SI                   65536
SF             125.8006086 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
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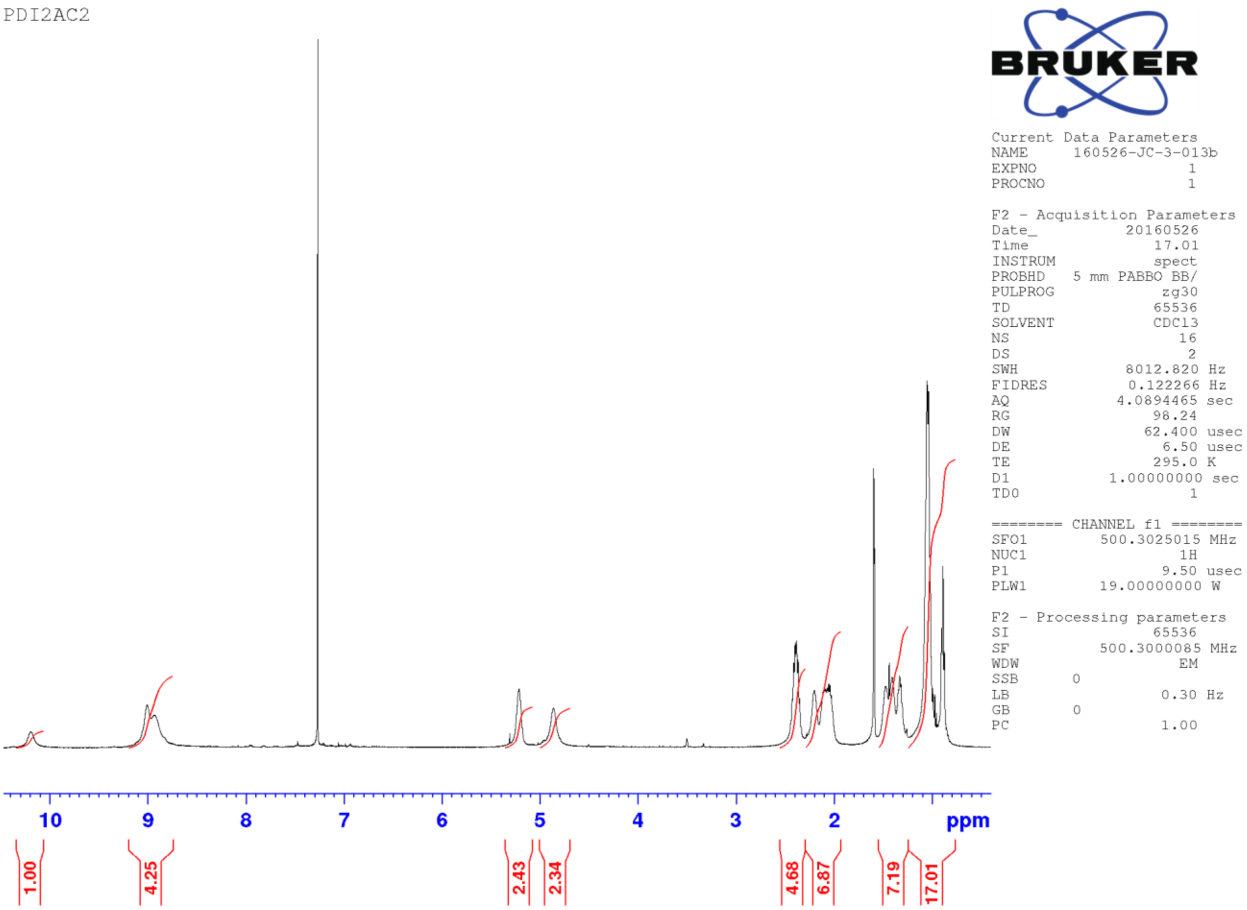
Figure S5. ^{13}C NMR of **PDI$_2$AC (4)**: **^{13}C NMR (CDCl$_3$):** 134.4, 131.6, 126.4, 123.9, 123.8, 121.9, 121.5, 119.0, 118.7, 118.6, 98.4, 57.5, 57.3, 46.5, 30.8, 26.4, 24.6, 21.9, 13.4.



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RG                   98.24
DW                  62.400 usec
DE                    6.50 usec
TE                   295.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           500.3025015 MHz
NUC1                    1H
P1                    9.50 usec
PLW1           19.00000000 W

F2 - Processing parameters
SI                   65536
SF             500.3000085 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
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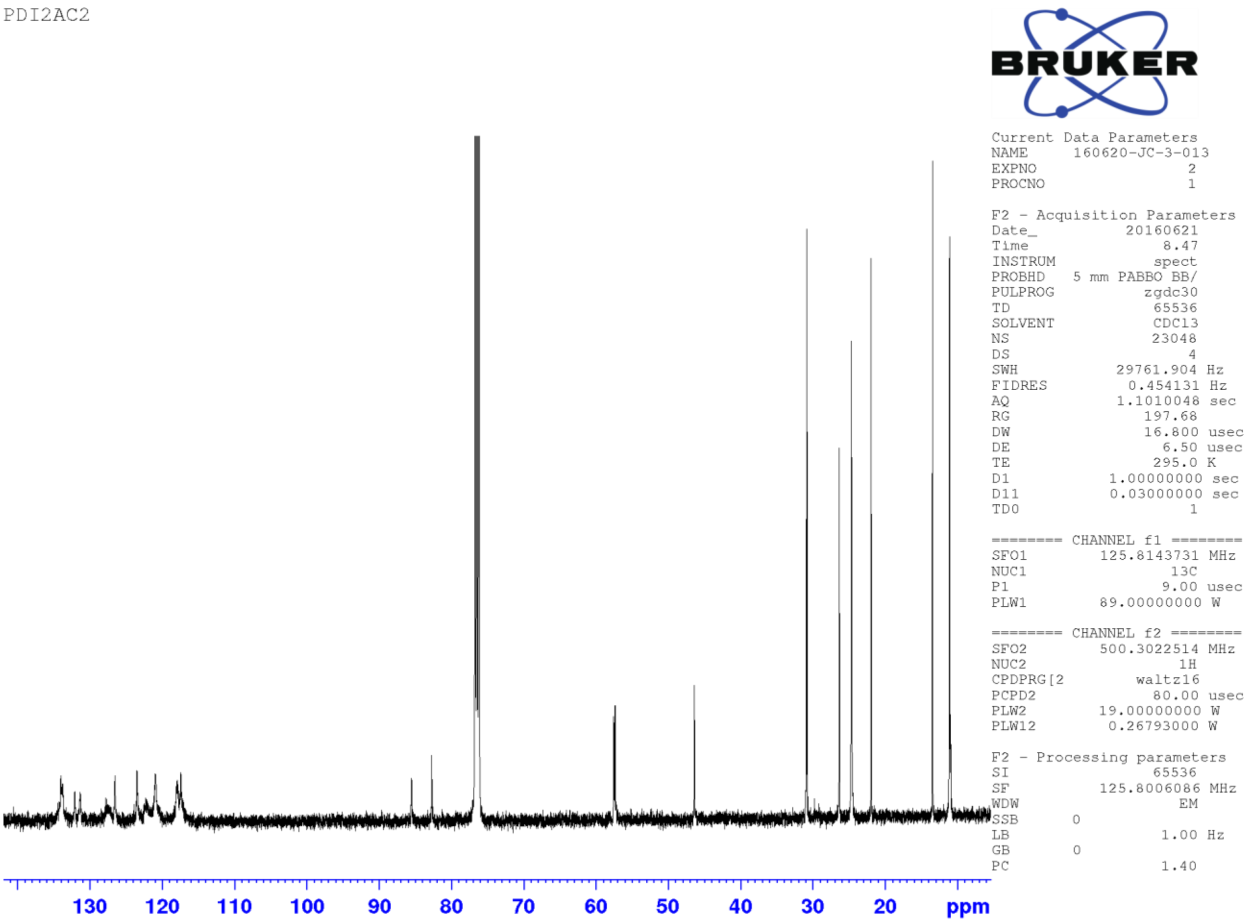
Figure S6. ^{1}H NMR of **PDI$_2$AC$_2$ (5)**: **^{1}HNMR (CDCl$_3$):** 10.29 (d, J$_{H-H}$ = 9 Hz, 2H); 9.16 (s, 2H); 9.07 (m, 6H); 5.24 (m, 4H); 4.94 (2, J$_{H-H}$ = 8 Hz, 4H); 2.4 (m, 8H); 2.25 (m, 4H); 2.04 (m, 8H); 1.53-1.26 (m, 12h); 1.59 (q, J$_{H-H}$ = 8 Hz, 18H); 0.89 (t, J$_{H-H}$ = 8 Hz, 6H).



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PROCNO                  1

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NS                  23048
DS                      4
SWH             29761.904 Hz
FIDRES           0.454131 Hz
AQ              1.1010048 sec
RG                 197.68
DW                 16.800 usec
DE                   6.50 usec
TE                  295.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         125.8143731 MHz
NUC1                 13C
P1                   9.00 usec
PLW1         89.00000000 W

======== CHANNEL f2 ========
SFO2         500.3022514 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2               80.00 usec
PLW2         19.00000000 W
PLW12         0.26793000 W

F2 - Processing parameters
SI                  65536
SF           125.8006086 MHz
WDW                    EM
SSB       0
LB                   1.00 Hz
GB        0
PC                   1.40
```

Figure S7. ^{13}C NMR of **PDI$_2$AC$_2$ (5)**: **^{13}CNMR (CDCl$_3$):** 134.0, 126.6, 123.5, 121.0, 117.9, 117.4, 85.5, 82.7, 57.5, 57.4, 46.4, 31.0, 30.8, 26.3, 24.7, 21.9, 13.4, 11.1, 11.0, 10.9.

Supplementary Crude ^{1}H NMR spectra.

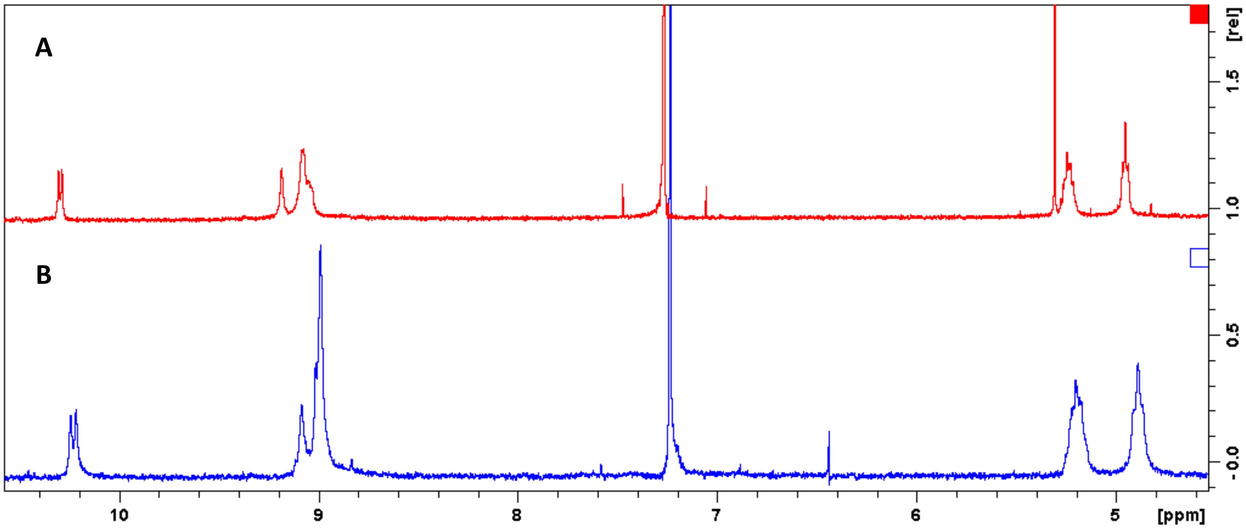


Figure S8: ^{1}H NMR spectra showing A) product obtained via decomposition of **2** and B) **5**

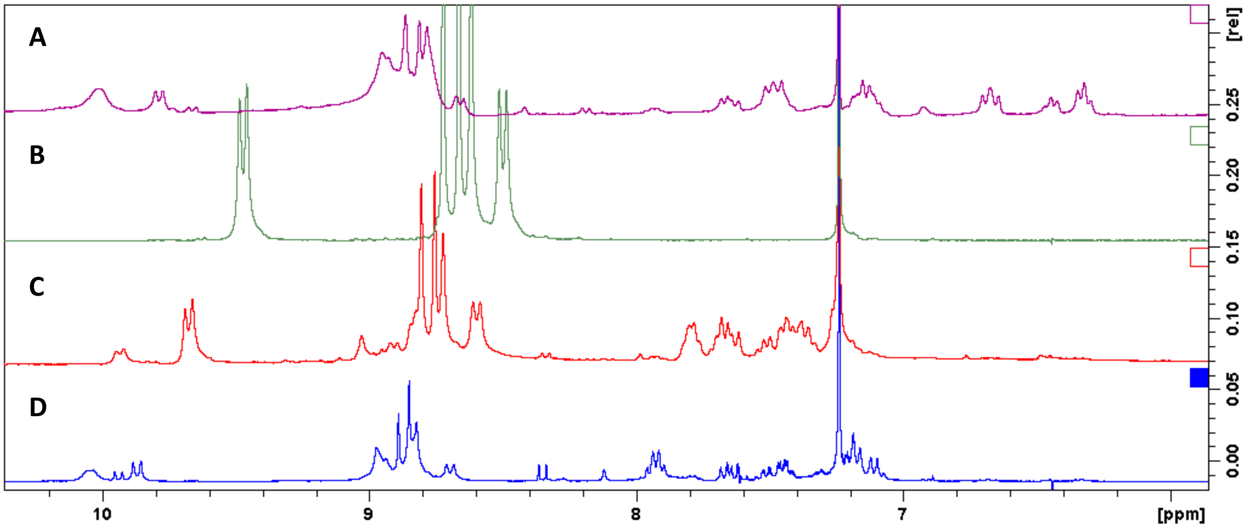


Figure S9: ^{1}H NMR spectra of Glaser homocoupling under A) air free conditions, B) copper free conditions, C) palladium free conditions, and D) standard conditions.

DFT Analysis:

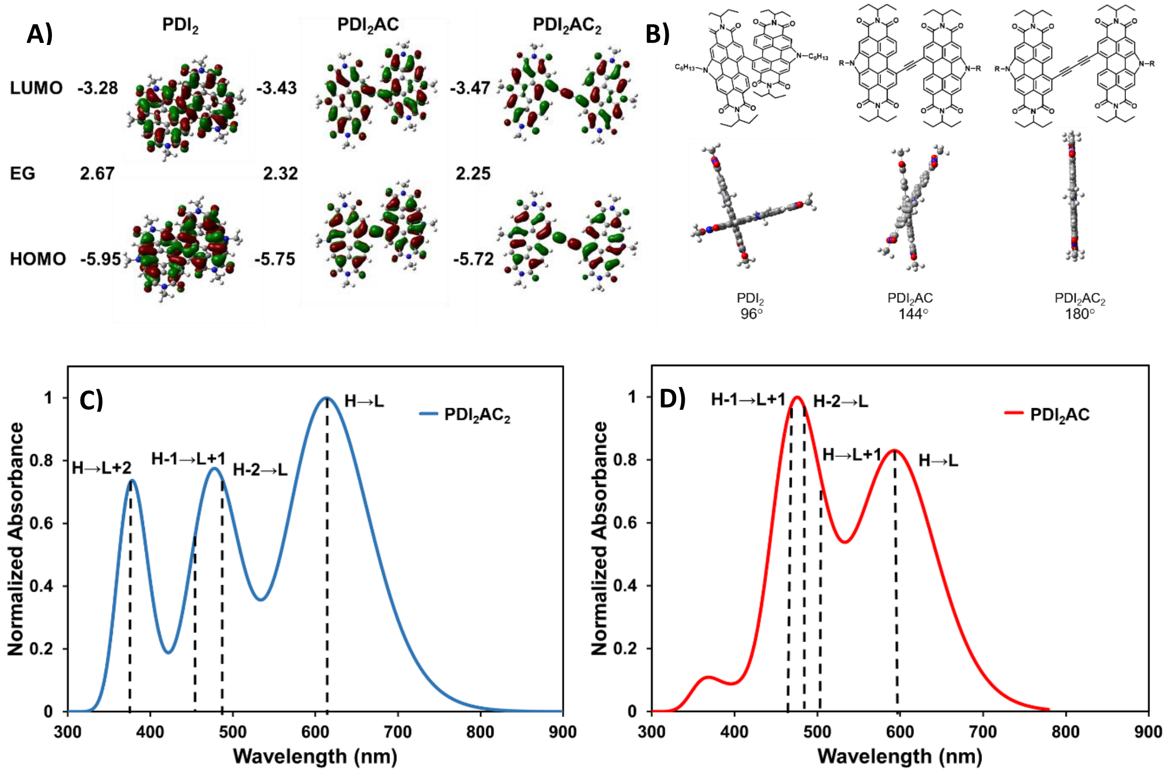


Figure S10: DFT analysis of A) frontier energy levels, B) twist angle, and predicted absorption of C) **4** and D) **5**

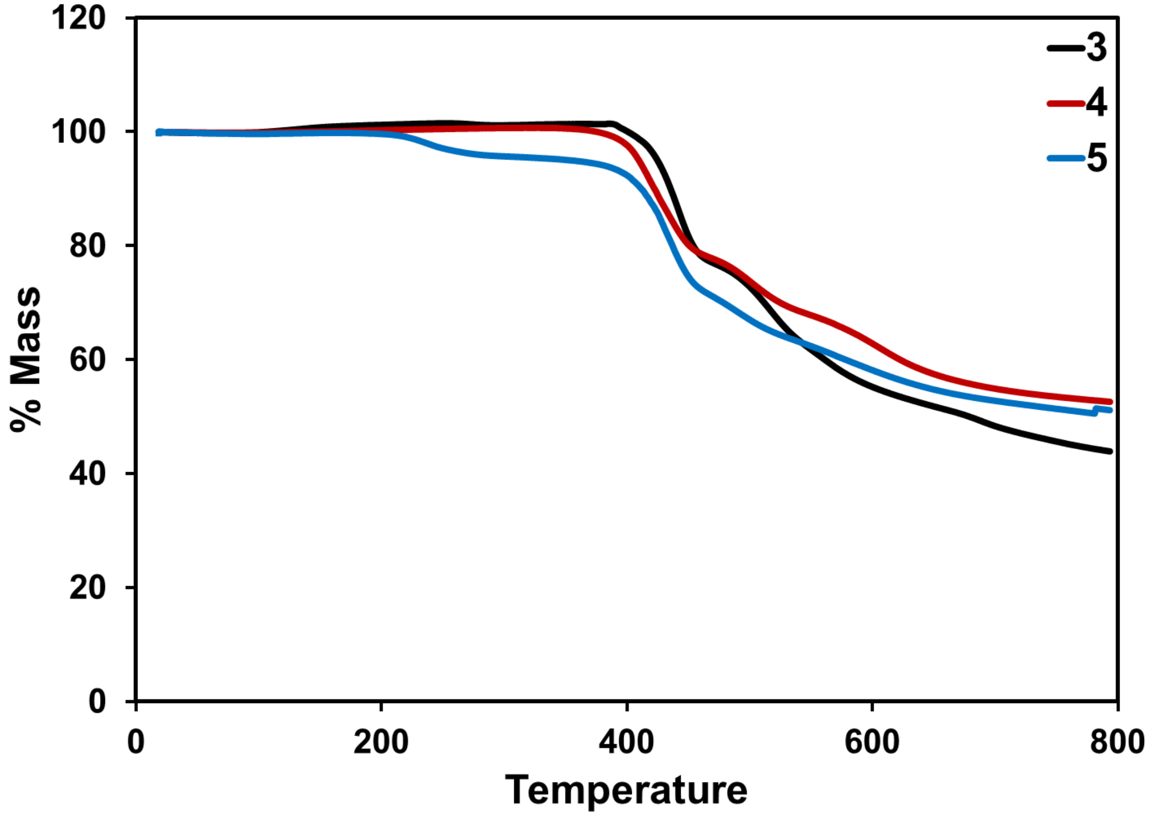


Figure S11: TGA plot of compounds **3**, **4** and **5**.

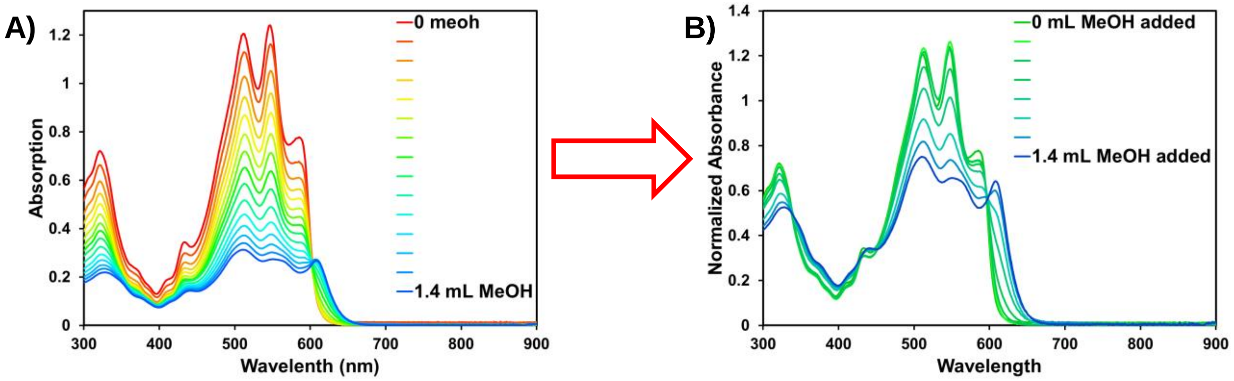


Figure S12. *UV-Visible spectra of* PDI$_2$Ac (**4**), at a concentration of 0.1 mg/mL titrated with 0.1 mL aliquots A) is raw data, B) is normalized against dilution and alternate traces were removed for clarity

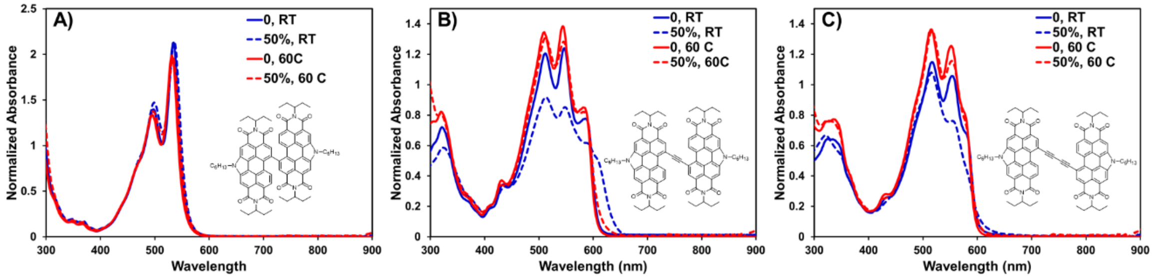


Figure S13. Normalized UV-vis spectra at room temperature and 60 °C of solutions in chloroform and 50% methanol of A) 3, B) 4, and C) 5.

Solar Cell Data.

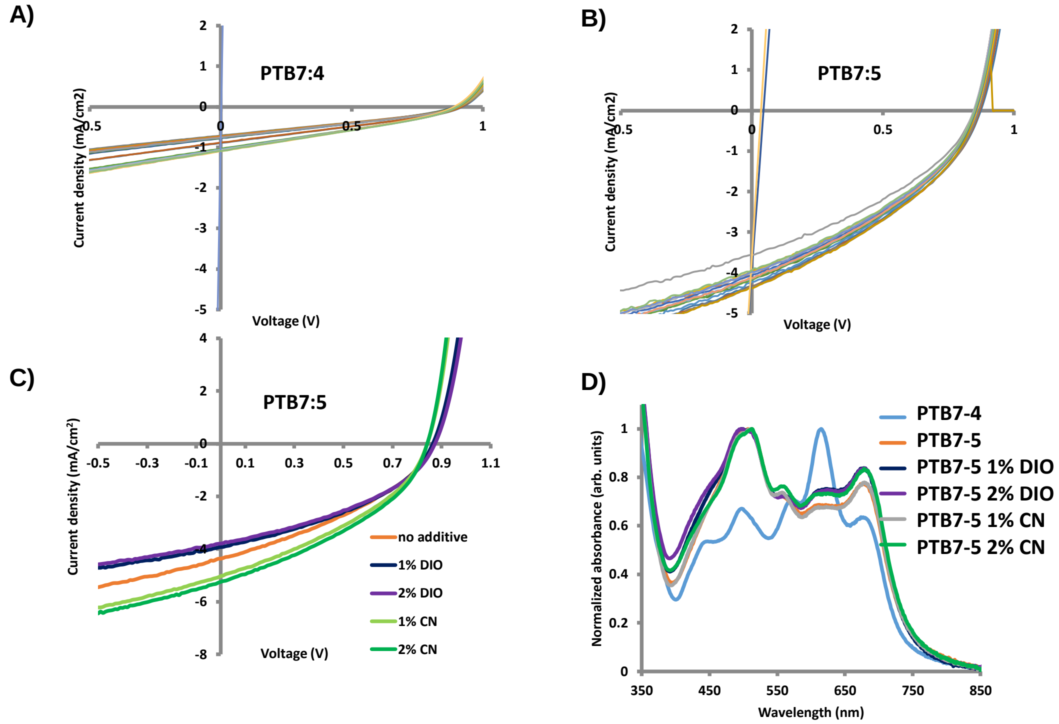


Figure S14: BHJ blends of PTB7 and PDI acceptors **4**, and **5** processed from chlorobenzene. All films as-cast. Device architecture used was ITO/Zno/BHJ/MoO$_x$/Ag. **A)** current density-voltage curves of PTB7:**4** based solar cells (poor PV performance was observed due to the low solubility of **4** in chlorobenzene, **B)** current density-voltage curves of PTB7:5 based solar cells, **C)** current density-voltage curves of PTB7:**5** based solar cells processed with solvent additives, **D)** optical absorption spectra of thin-film blends.

Table S1: Photovoltaic parameters for the optimization of PTB7:**5** based solar cell devices. All films processed from 1:1 weight ratio solutions from chlorobenzene. Device architecture = ITO/ZnO/BHJ/MoO$_x$/Ag.

additive	**Voc (V)**	**Jsc (mA/cm^2)**	**Pmax (mW/cm^2)**	**FF**	
none	**0.85**	**-4.11**	**-1.28**	**0.36**	**avg.**
	0.87	**-4.36**	**-1.37**	**0.36**	**best**
1% DIO	**0.86**	**-3.85**	**-1.29**	**0.39**	**avg.**
	0.86	**-3.94**	**-1.34**	**0.40**	**best**
2% DIO	**0.86**	**-3.72**	**-1.26**	**0.39**	**avg.**
	0.87	**-3.81**	**-1.31**	**0.40**	**best**
1% CN	**0.85**	**-4.87**	**-1.51**	**0.37**	**avg.**
	0.84	**-5.03**	**-1.58**	**0.37**	**best**
2% CN	**0.84**	**-4.98**	**-1.55**	**0.37**	**avg.**
	0.84	**-5.24**	**-1.68**	**0.38**	**best**

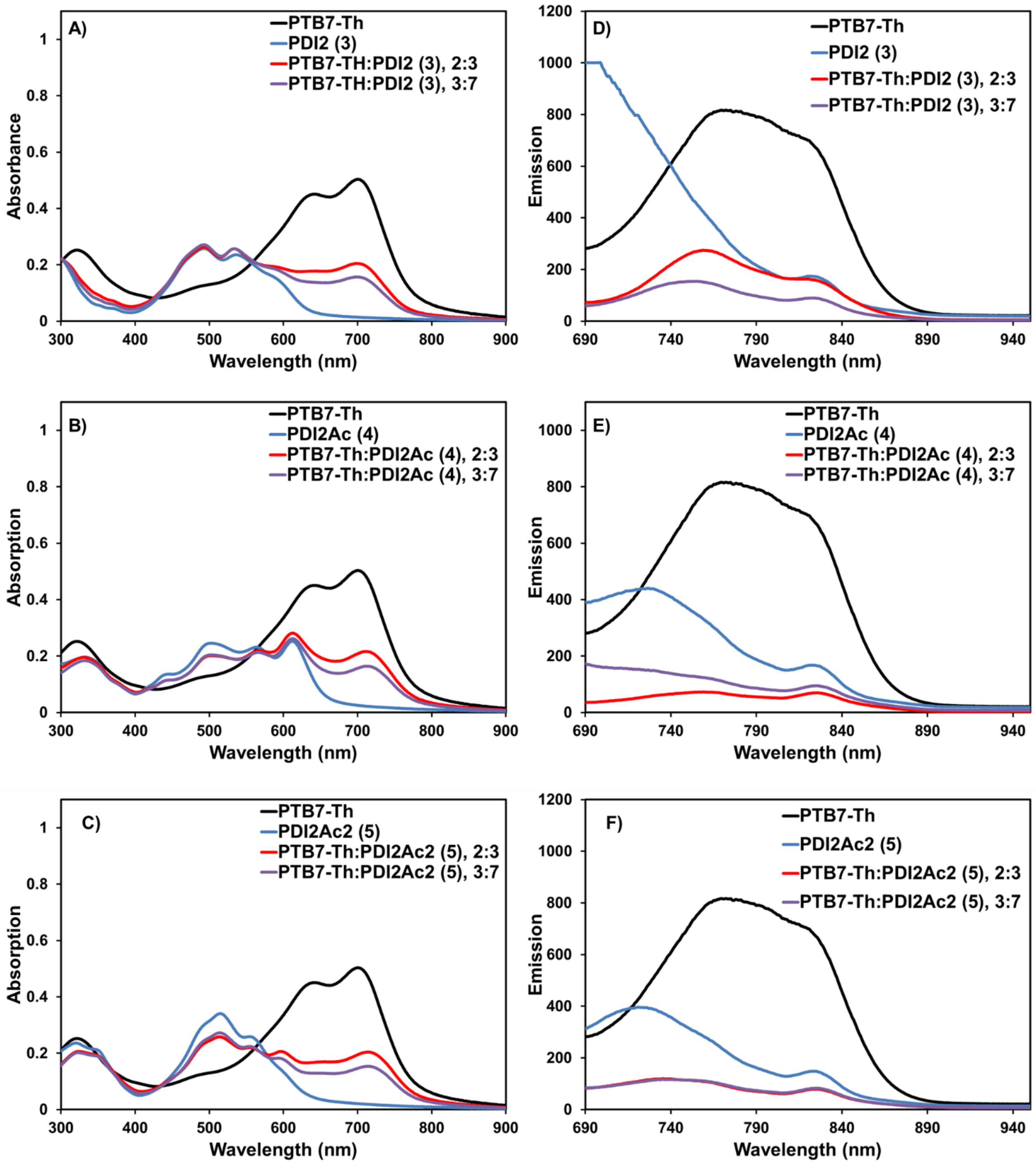


Figure S15: UV-vis spectra of blends of PTB7-Th with A) **3**, B) **4**, and C) **5**, as well as fluorescence of blends of PTB7-Th with D) **3**, E) **4** and F) **5**. All films formed from 10 mg/mL total solids $CHCl_3$ solutions.

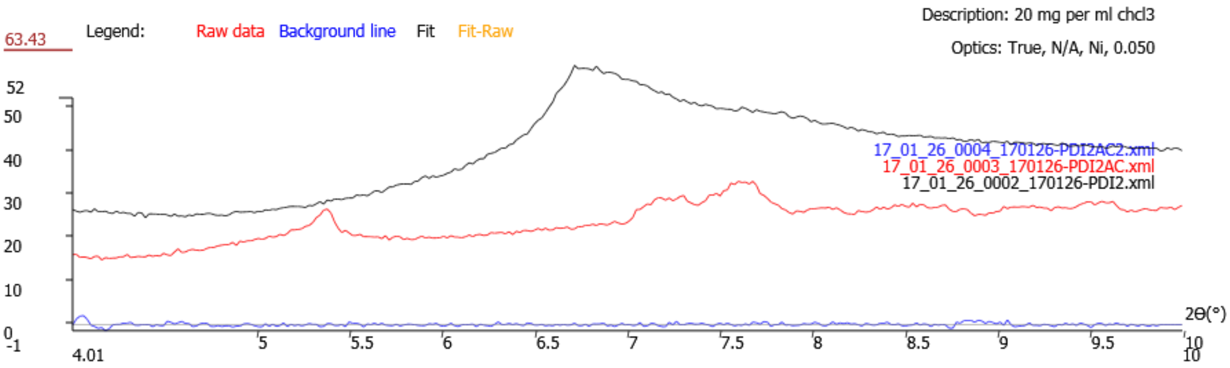
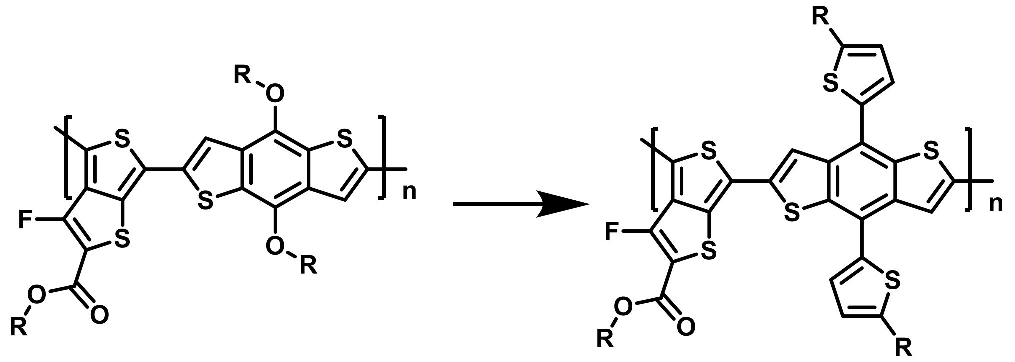


Figure S16: Powder XRD of films drop cast from 20 µL of 20 mg/mL solutions of **3** (black), **4** (red), and **5** (blue)



PTB7
R= Ethylhexyl

PTB7-Th
R= Ethylhexyl

Figure S17: Structures of PTB7 and PTB7-Th