SUPPORTING INFORMATION

A Narrow Band Gap Isoindigo Based Molecular Donor for Solution Processed Organic Solar Cells

Jetsuda Areephong,[a] Ronan R. San Juan,[a] Abby-Jo Payne [a] and Gregory C. Welch[a]*

Department of Chemistry Dalhousie University, 6274 Coburg Road, Halifax, Nova Scotia,
Canada B3H 4R2.

*corresponding author: gregory.welch@dal.ca

NEW JOURNAL OF CHEMISTRY

Experimental

Materials: All chemicals were purchased commercially and used as received. DTS(FBT-Th-Th_{HEX})$_2$) was obtained from 1-Material. PEDOT:PSS (768642-25G), $PC_{61}BM$ (684430-1G), anhydrous $CHCl_3$, xylene, and chlorobenzene were purchased from Sigma-Aldrich and used as received.

Methods: NMR spectroscopy, differential scanning calorimetry, UV-Vis absorption and emission spectroscopy, X-ray diffraction, and cyclic voltammetry were all carried out as previously reported. (see: S. M. McAfee, J. M. Topple, A.-J. Payne, J.-P. Sun, I. G. Hill and G. C. Welch, *ChemPhysChem*, 2014, DOI: 10.1002/cphc.201402662)

Atomic Force Microscopy (AFM): AFM images were obtained using a Bruker Innova atomic force microscope run in tapping mode with NCHV-A tips with resonant frequencies ~320 kHz. The AFM images were collected over 20μm×20μm and 5μm×5μm scan areas using a scan rate of 0.75 Hz, a scanning resolution of 256 samples per line. Images were collected using NanoScope Analysis software.

External Quantum Efficiency (EQE) or Incident Photon Conversion to Electron (IPCE) Analysis: Incident Photon Conversion Efficiency spectra were recorded using a 150 W Xe source, optical chopper wheel, monochromator (Oriel Cornerstone 260 1/4 m), lock-in amplifier, and a calibrated silicon photodiode (Newport 818-UV-L). Various long-pass filters were used to reduce second order transmission through the monochromator.

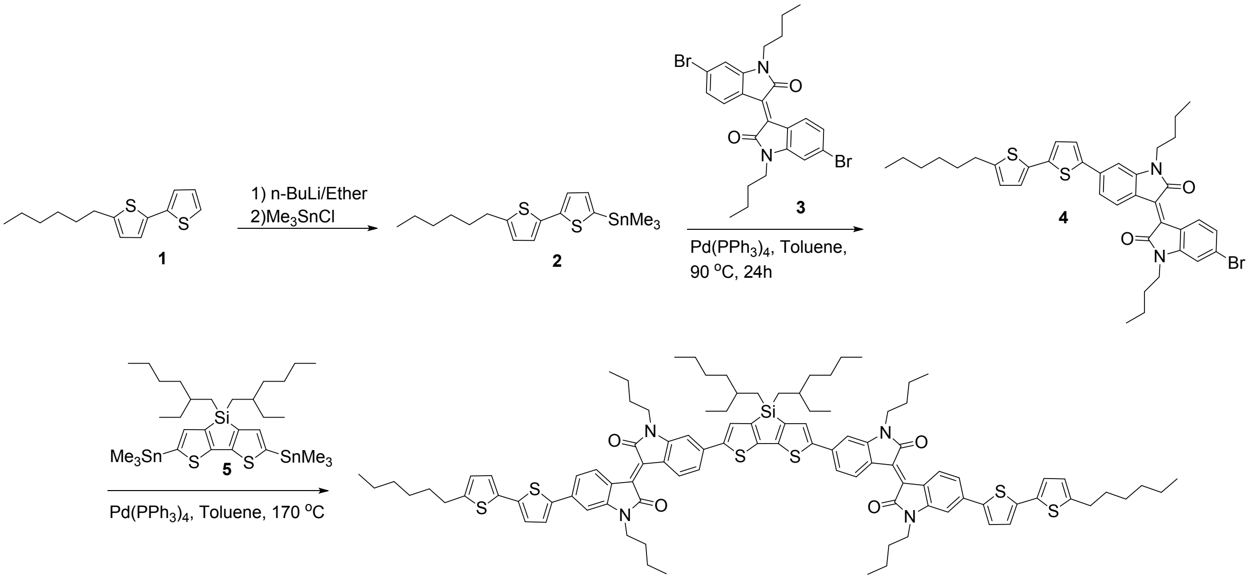
Device Fabrication: Device fabrication was simialr to previously reported. (see: S. M. McAfee, J. M. Topple, A.-J. Payne, J.-P. Sun, I. G. Hill and G. C. Welch, *ChemPhysChem*, 2014, DOI: 10.1002/cphc.201402662). The devices were prepared on cleaned, UV/ozone-treated Corning glass patterned with ITO (substrate size 15x15 mm), upon which the conductive polymer PEDOT:PSS was spin casted at 5000 rpm for 60 seconds. The $DTS(IIThTh_{HEX})_2/PC_{61}BM$ active layers were prepared from solutions at an overall concentration of 30 mg mL^{-1}. The solutions were heated for several hours and residual solids were quickly filtered prior to casting at 80°C (xylene solutions) or 50°C ($CHCl_3$ solutions) under inert atmosphere (1500 rpm for 60 seconds). Cathodes were deposited by sequential thermal evaporation of 7.5 nm Ca followed by 100 nm Al. Device size was 0.11 cm^2 with two devices per substrate. Minimum of six devices were measured for each condition. Eight devices were measured for the top performing chloroform/DIO processing conditions. Device characteristics were measured under illumination by a simulated 100 mW cm^{-2} AM1.5G light source using a 300 W Xe arc lamp with an AM 1.5 global filter. Solar-simulator irradiance was calibrated using a standard silicon photovoltaic detector.

Control devices with a $DTS(FBTTh_2)_2/PC_{61}BM$ active layer were fabricated following our previously mentioned conditions which are similar to the original reports. PCEs from 4-5% were routinely obtained.

Theoretical Calculations. Calculations were performed as previously described (see: *J. Phys. Chem. A*, 2014, 118 (36), pp 7939–7951)

Synthesis and Characterization

The synthesis of DTS(IIThTh$_{\mathrm{HEX}}$)$_2$ is shown in Scheme S1. The Stille cross-coupling between 6,6'-dibromo-N-N'-butyl-isoindigo (**3**) and trimethyl stannyl-bithiophene (**2**) yielded the intermediate **4** in reasonable yield (60%). Target molecule DTS(IIThTh$_{\mathrm{HEX}}$)$_2$ was successfully synthesized via Stille Coupling of both **4** and **5** in moderated yield (74%) through a conventional heat at 110 ˚C for 24 h. Though we further investigated the Stile coupling between **4** and **5** via a microwave irradiation at 170 ˚C for 40 min, only 30% of desired product was obtained.



Scheme 1. Synthesis DTS(IIThTh$_{\mathrm{HEX}}$)$_2$ **Compound 2:** An n-BuLi solution (2.5 M in hexane, 2.8 mL, 6.9 mmol) was added to a solution of **1** (1.17 g, 4.7 mmol) in dry ether (20 mL) at -78 ˚C. The reaction mixture was stirred at -78 ˚C for one hour, and then at room temperature for one hour, followed by adding a solution of trimethyltinchloride (1.4g, 6.9 mmol) in dry ether (5mL) at -78 ˚C. The reaction was stirred overnight at room temperature. The mixture was washed with water and brine. The organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to obtain compound **2** (1.9 g, 99%). The crude product was used without further purification. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ 7.22 (d, J= 3.3 Hz, 1H), 7.08 (d, J= 3.3 Hz, 1H), 6.98 (d, J= 3.5 Hz, 1H), 6.68 (d, J= 3.3 Hz, 1H), 2.80 (t, J= 7.5 Hz, 2H), 1.44-1.28 (m, 8H), 0.91 (t, J= 7.5 Hz, 3H), 0.40 (s, 9H)

Compound 3: A 10-20 mL glass tube equipped with a stir bar was charged with 6,6'-dibromoisoindigo[1] (0.5g, 1.2 mmol), K_2CO_3 (0.49 g, 3.6 mmol) and DMF (10 mL) and sealed with a Teflon® cap under nitrogen. 1-Bromobutane (0.37 g, 2.7 mmol) was added via syringe. The reaction mixture was heated to 120 ˚C for 25 minutes using a Biotage microwave reactor. The dark-red solution was poured into water (500 mL) and stirred for one hour. The red solid was filtered and recrystallized in isopropanol to obtain desired product **3** in 0.56 g (88%). ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K) δ 9.09 (d, J= 8.6 Hz, 2H), 7.18 (dd, J= 3.5, 1.8 Hz, 2H), 6.94 (d, J= 1.8 Hz, 2H), 3.76 (t, J= 7.3 Hz, 4H), 1.72 (m, 4H), 1.48 (m, 4H), 0.99 (t, J= 7.3 Hz, 6H) ^{13}C NMR

(CDCl$_3$, 75 MHz, 298 K): δ 167.75, 145.79, 132.64, 131.21, 126.73, 125.14, 120.43, 111.30, 40.02, 29.44, 20.24, 13.73 MS(APCI) *m/z*, calcd for $C_{24}H_{24}Br_2N_2O_2$ (M+H): 533.0; found: 533.0

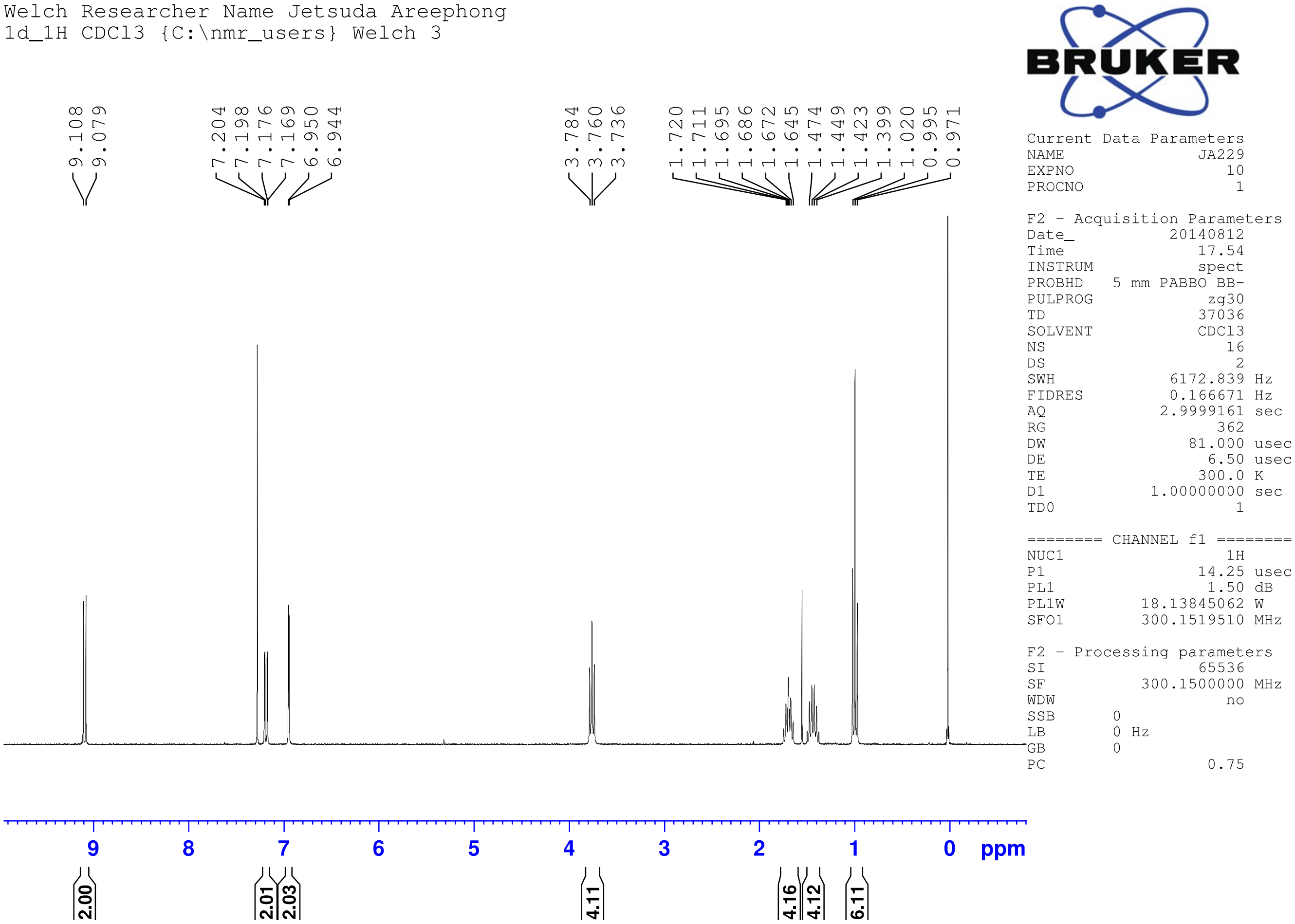
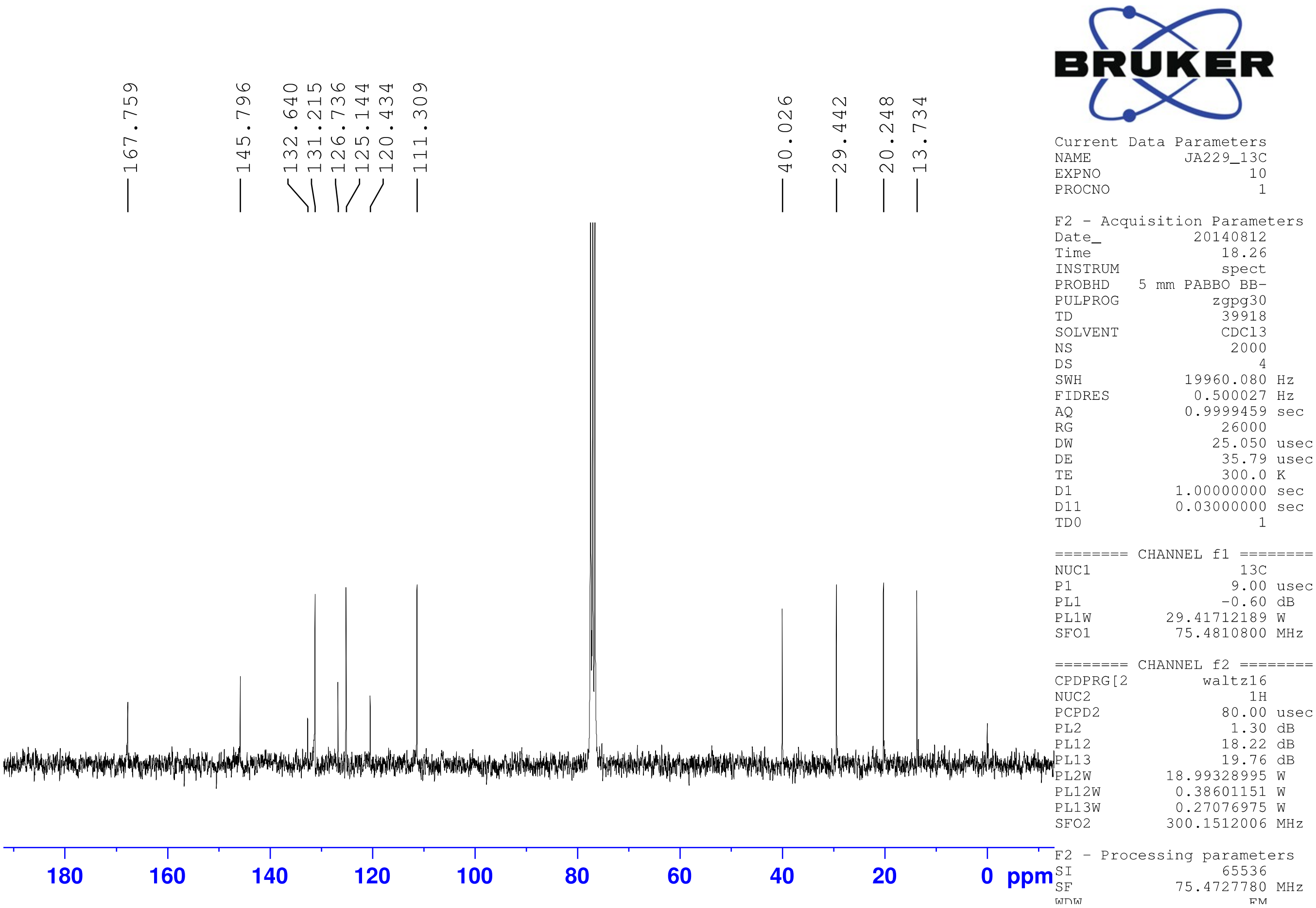


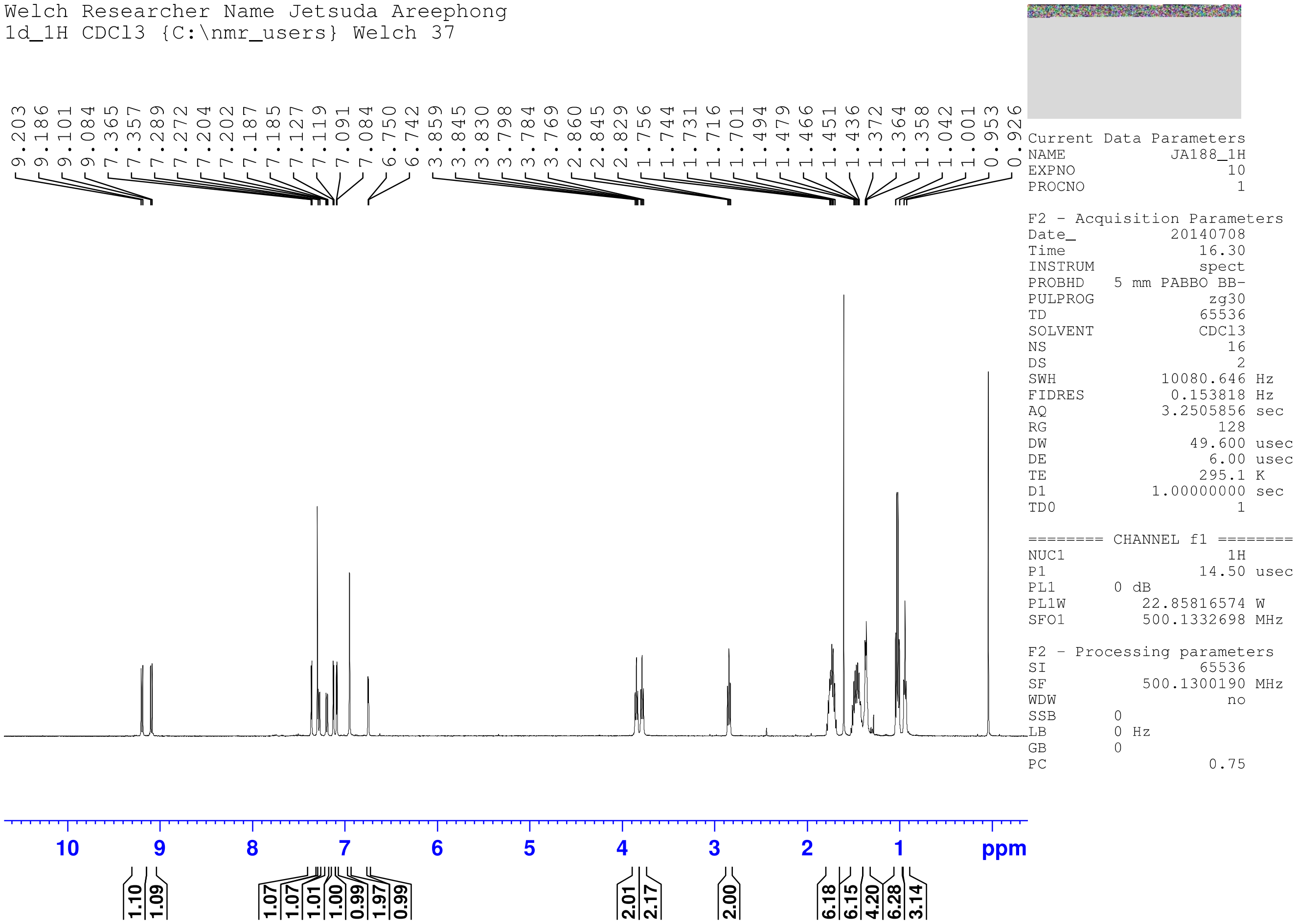
Figure S1. ^{1}H NMR spectrum of compound **3** in CDCl$_3$



```
Current Data Parameters
NAME             JA229_13C
EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140812
Time                 18.26
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                  39918
SOLVENT             CDCl3
NS                   2000
DS                      4
SWH             19960.080 Hz
FIDRES           0.500027 Hz
AQ              0.9999459 sec
RG                  26000
DW                 25.050 usec
DE                  35.79 usec
TE                  300.0 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.00 usec
PL1                 -0.60 dB
PL1W          29.41712189 W
SFO1           75.4810800 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                  1.30 dB
PL12                18.22 dB
PL13                19.76 dB
PL2W          18.99328995 W
PL12W          0.38601151 W
PL13W          0.27076975 W
SFO2          300.1512006 MHz

F2 - Processing parameters
SI                  65536
SF             75.4727780 MHz
```

Figure S2. ^{13}C NMR spectrum of compound **3** in $CDCl_3$

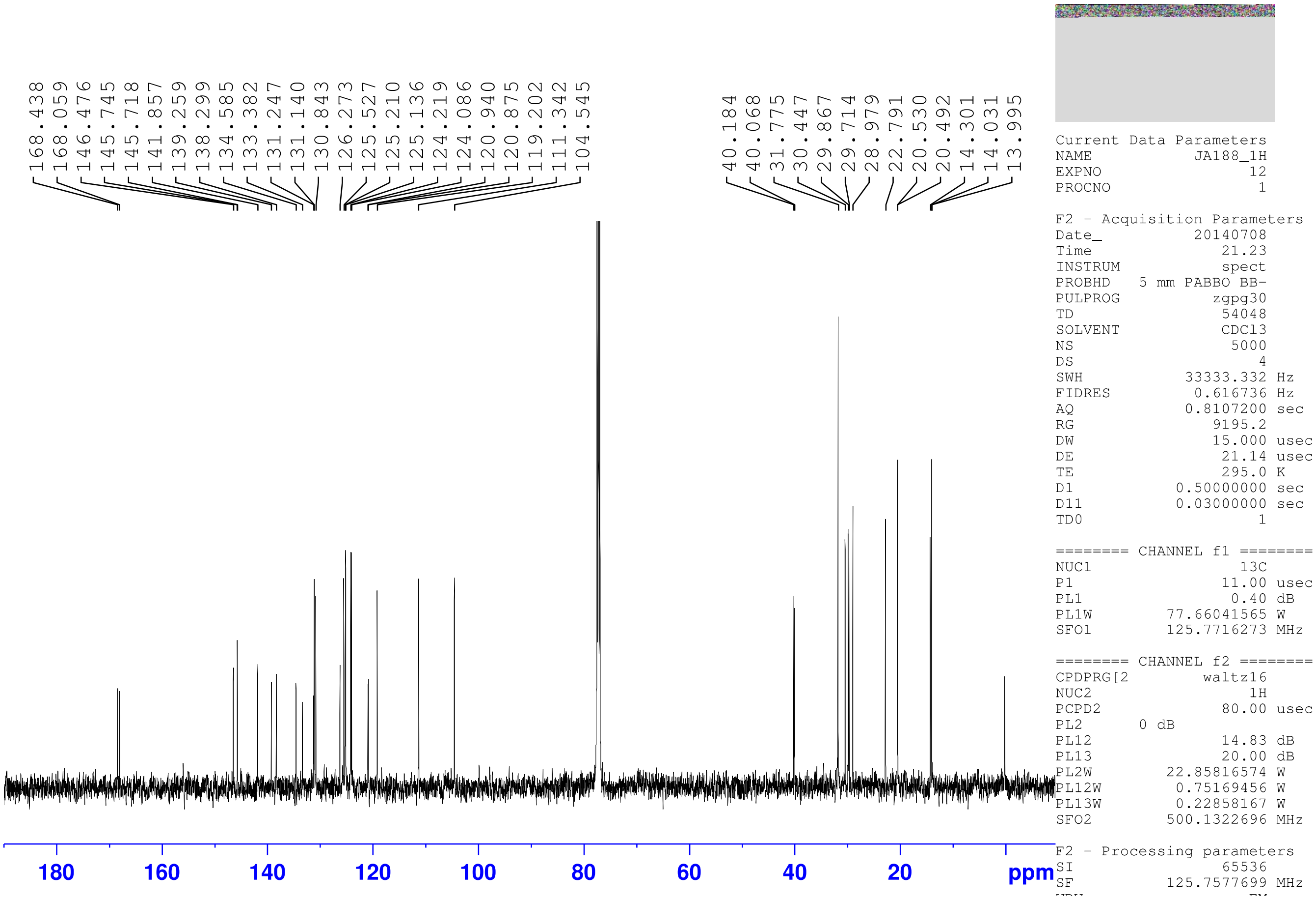
Compound 4: A 10-20 mL glass tube equipped with a stir bar was charged with **2** (0.18 g, 0.45 mmol), 2-(Tributylstannyl)thiophene (1.14 mL, 3.6 mmol), $Pd(PPh_3)_4$ (38 mg, 2 mol %), anhydrous toluene (10 mL) and sealed with a Teflon® cap under nitrogen. The reaction mixture was heated at 90°C for 24 hours. Upon cooling, the reaction mixture was diluted with DCM (100 mL). The organic phase was stirred in a 1:5 mixture of K_2CO_3:SiO_2 (to trap Sn by-product) then filtered through a short plug of silica gel. The organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The crude product **4** was purified by silica flash column chromatography using pentane/DCM gradient to obtain **4** as dark purple solid in 187 mg (61%). ^{1}H NMR ($CDCl_3$, 500 MHz, 298 K) δ 9.19 (d, J= 8.4 Hz, 1H), 9.09 (d, J= 8.5Hz, 1H), 7.36 (d, J= 3.8 Hz, 1H), 7.28 (m, 1H), 7.19 (dd, J= 8.5, 1.2 Hz, 1H), 7.12 (d, J= 3.8 Hz, 1H), 7.08 (d, J= 3.5 Hz, 1H), 6.94 (s, 2H), 6.74 (d, J= 3.5 Hz, 1H), 3.84 (t, J= 7.3 Hz, 2H), 3.78 (t, J= 7.3 Hz, 2H), 2.84 (t, J= 7.6 Hz, 2H), 1.77-1.70 (m, 6H), 1.51-1.34 (m, 10H), 1.04-1.01 (m, 6H), 0.93 (t, J=6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz, 298 K) δ 168.44, 168.06, 146.48, 145.74, 145.72, 141.86, 139.26, 138.30, 134.58, 133.38, 131.25, 131.14, 130.84, 126.27, 125.52, 125.21, 125.13, 124.22, 124.08, 120.94, 120.87, 119.20, 111.34, 104.54, 40.18, 40.07, 31.77, 30.44, 29.87, 29.71, 28.97, 22.79, 20.53, 20.49, 14.30, 14.03, 13.99. MS(APCI) *m/z*, calcd for $C_{38}H_{41}BrN_2O_2S_2$ (M+H): 701.2; found: 701.2



```
Welch Researcher Name Jetsuda Areephong
1d_1H CDCl3 {C:\nmr_users} Welch 37
```

```
Current Data Parameters
NAME            JA188_1H
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140708
Time               16.30
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10080.646 Hz
FIDRES          0.153818 Hz
AQ             3.2505856 sec
RG                   128
DW                49.600 usec
DE                  6.00 usec
TE                 295.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.50 usec
PL1         0 dB
PL1W         22.85816574 W
SFO1         500.1332698 MHz

F2 - Processing parameters
SI                 65536
SF           500.1300190 MHz
WDW                   no
SSB         0
LB          0 Hz
GB          0
PC                  0.75
```

Figure S3. ^{1}H NMR spectrum of compound **4** in $CDCl_3$



```
Current Data Parameters
NAME             JA188_1H
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140708
Time                21.23
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  54048
SOLVENT             CDCl3
NS                   5000
DS                      4
SWH             33333.332 Hz
FIDRES           0.616736 Hz
AQ              0.8107200 sec
RG                 9195.2
DW                 15.000 usec
DE                  21.14 usec
TE                  295.0 K
D1             0.50000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  11.00 usec
PL1                  0.40 dB
PL1W          77.66041565 W
SFO1          125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2        0 dB
PL12                14.83 dB
PL13                20.00 dB
PL2W          22.85816574 W
PL12W          0.75169456 W
PL13W          0.22858167 W
SFO2          500.1322696 MHz

F2 - Processing parameters
SI                  65536
SF            125.7577699 MHz
```

Figure S4. ^{13}C NMR spectrum of compound **4** in $CDCl_3$

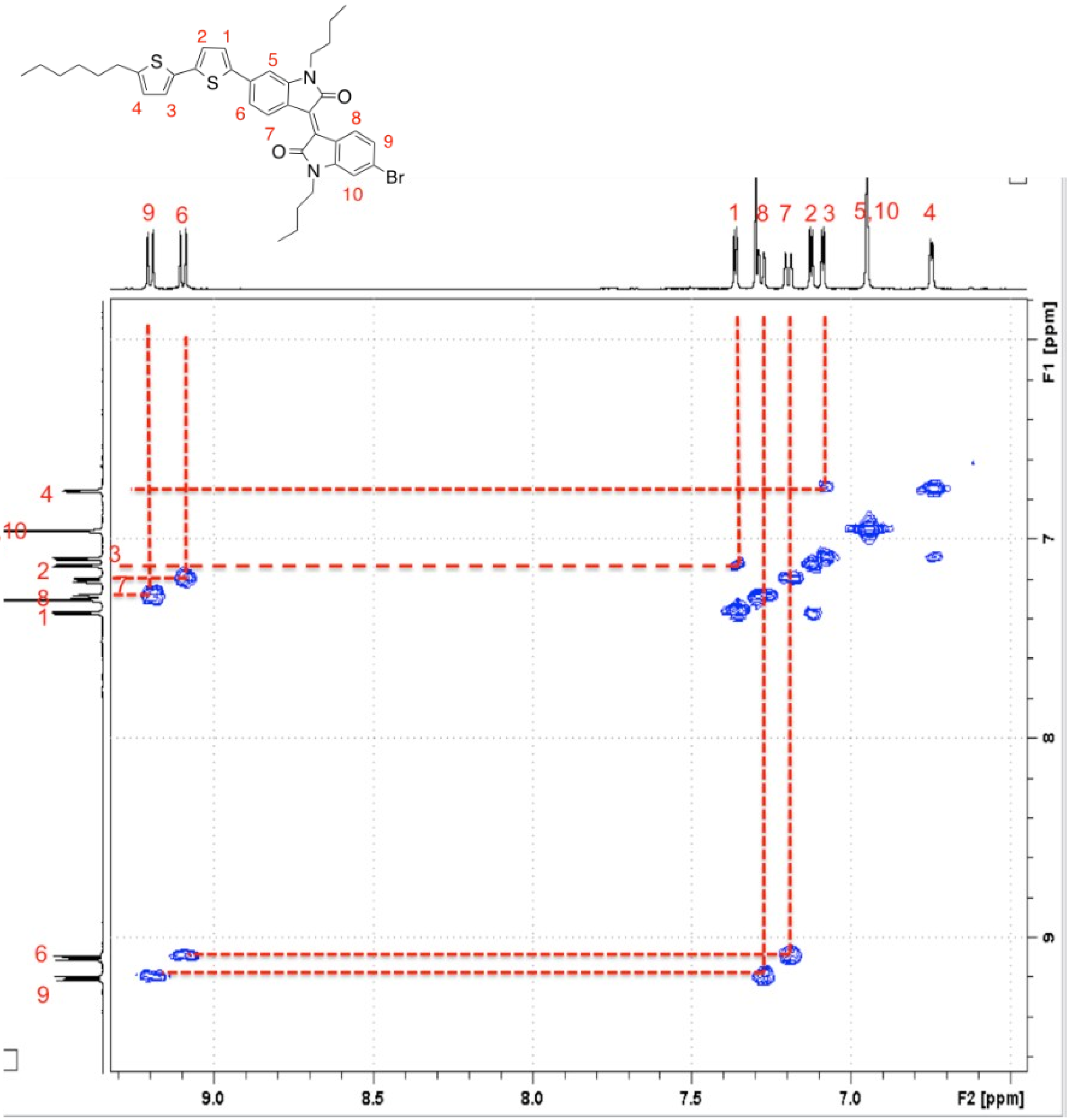
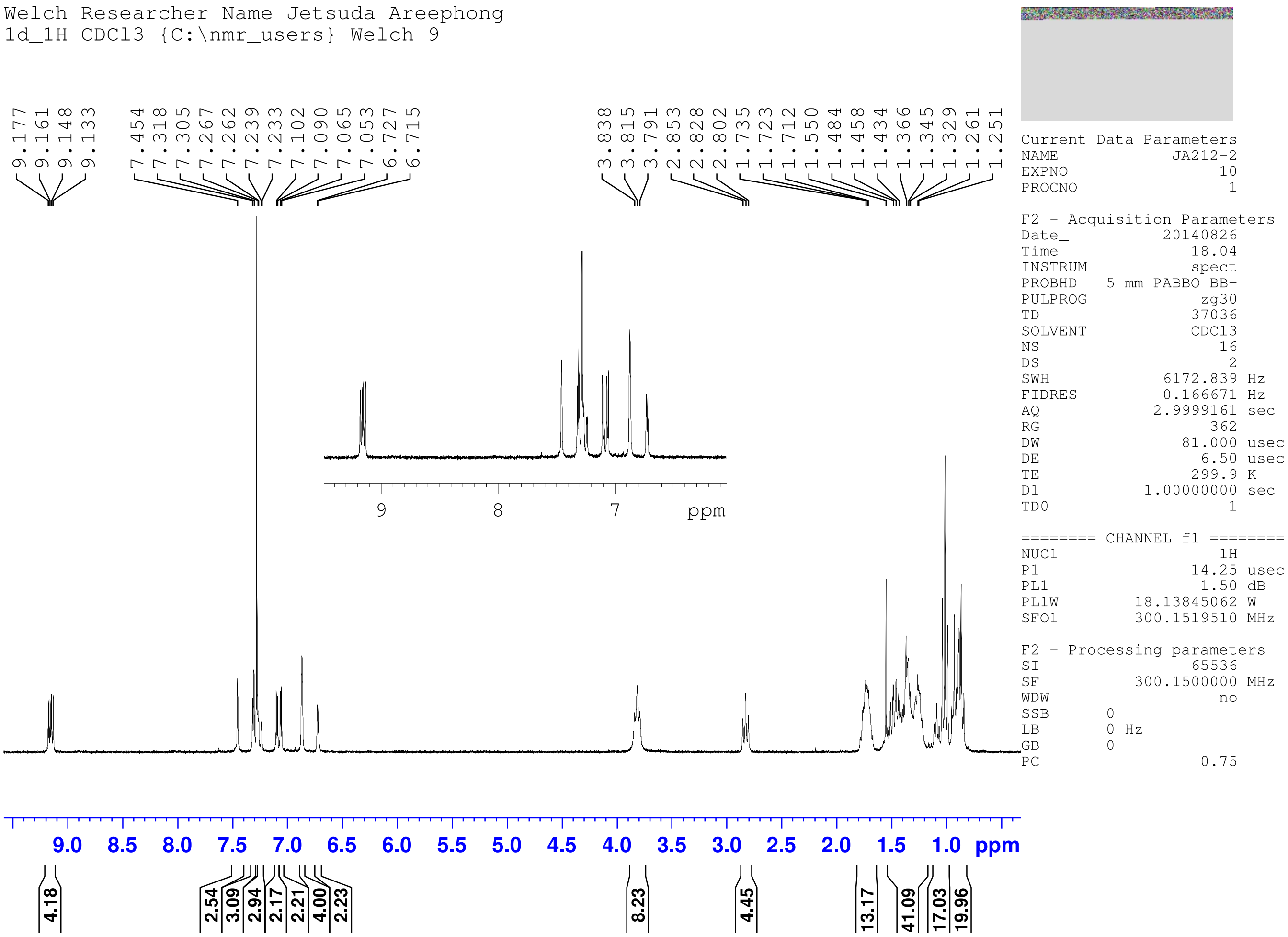


Figure S5. 2D COSY-NMR spectrum of compound **4** in $CDCl_3$

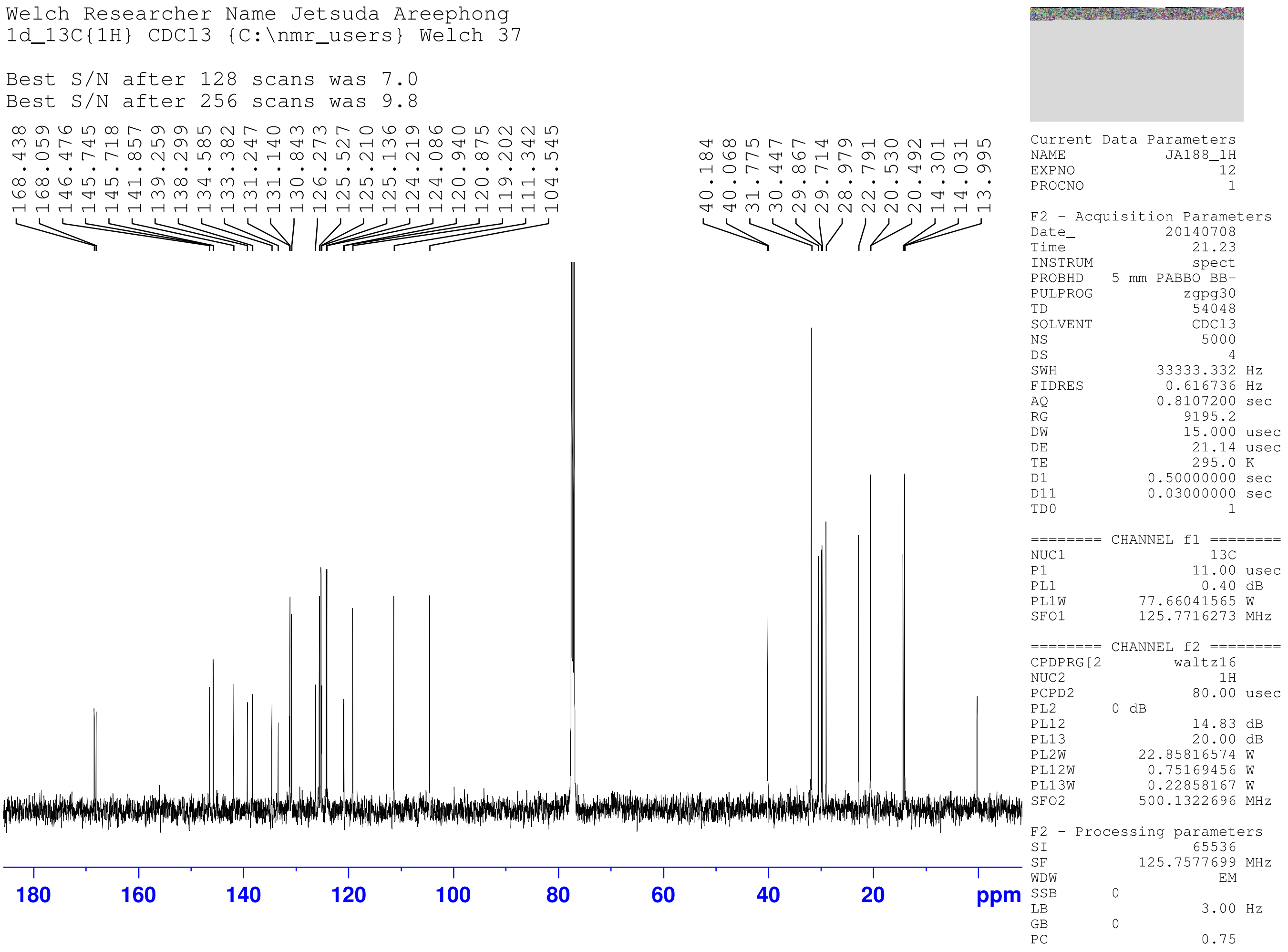
DTS(IIThTh$_{\mathbf{HEX}}$)$_2$: In a N_2 filled glove box, a 100 mL RBF was charged with **5**[2] (300 mg, 0.40 mmol), and **4** (600 mg, 0.85 mmol), $Pd(PPh_3)_4$ (50 mg, 0.04 mmol), toluene (50 mL), and sealed with a rubber septum. The reaction mixture was heated to 110 °C for 24 hours. Upon cooling and diluting in dichloromethane, a 5:1 SiO_2:K_2CO_3 mixture was added. The material was then filtered and the solvents were removed in vacuum. The crude product was purified by silica gel column chromatography using a pentane/dichloromethane gradient. The product eluted as a dark blue solution. After fraction collection and solvent removal, the product was slurried in 3:1 methanol:hexane, stirred for one hour and filtered and collected as a bronzy powder in 500 mg (75%). ^{1}H NMR (CDCl3, 500 MHz, 298 K) δ 9.15 (dd, J= 8.5, 8.5 Hz, 4H), 7.47 (s, 2H), 7.30 (s, 2H), 7.25 (m, 2H), 7.08 (d, J= 3.5 Hz, 4H), 6.84 (s, 4H), 6.73 (d, J= 3.1 Hz, 2H), 3.81 (m, 8H), 2.84 (t, J= 7.5 Hz, 4H), 1.73 (m, 12H), 1.49-1.26 (m, 38H), 1.17 (m, 4H), 1.02 (m, 12H), 0.94-0.88 (m, 18H). ^{13}C NMR (CDCl3, 125 MHz, 298 K) δ 168.50, 149.52, 146.32, 145.97, 145.47, 145.36, 142.16, 138.96, 138.03, 137.56, 134.72, 131.71, 131.53, 130.61, 130.54, 127.58, 125.26, 125.17, 124.18, 124.00, 121.28, 121.14, 118.97, 118.87, 104.52, 104.38, 40.00, 36.24, 35.94, 30.46, 29.94, 29.21, 29.17, 29.00, 23.29, 22.80, 17.96, 14.43, 14.29, 11.09. Elemental analysis: Calcd. C 72.33, H 7.16, 3.37, found C 71.78, H 7.00, N 3.31.



```
Welch Researcher Name Jetsuda Areephong
1d_1H CDCl3 {C:\nmr_users} Welch 9
```

```
Current Data Parameters
NAME              JA212-2
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140826
Time                18.04
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  37036
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6172.839 Hz
FIDRES           0.166671 Hz
AQ              2.9999161 sec
RG                    362
DW                 81.000 usec
DE                   6.50 usec
TE                  299.9 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  14.25 usec
PL1                  1.50 dB
PL1W          18.13845062 W
SFO1          300.1519510 MHz

F2 - Processing parameters
SI                  65536
SF            300.1500000 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   0.75
```

Figure S6. ^{1}H NMR spectrum of DTS(IIThTh$_{HEX}$)$_2$ in CDCl$_3$

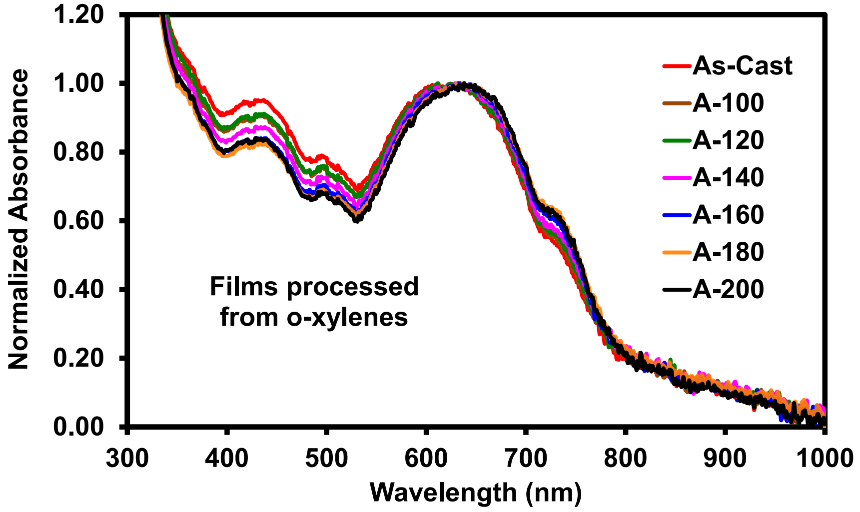


```
Welch Researcher Name Jetsuda Areephong
1d_13C{1H} CDCl3 {C:\nmr_users} Welch 37

Best S/N after 128 scans was 7.0
Best S/N after 256 scans was 9.8
```

```
Current Data Parameters
NAME              JA188_1H
EXPNO                   12
PROCNO                   1

F2 - Acquisition Parameters
Date_             20140708
Time                 21.23
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG            zgpg30
TD                   54048
SOLVENT              CDCl3
NS                    5000
DS                       4
SWH              33333.332 Hz
FIDRES            0.616736 Hz
AQ               0.8107200 sec
RG                  9195.2
DW                  15.000 usec
DE                   21.14 usec
TE                   295.0 K
D1              0.50000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   11.00 usec
PL1                   0.40 dB
PL1W           77.66041565 W
SFO1           125.7716273 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2       0 dB
PL12                 14.83 dB
PL13                 20.00 dB
PL2W           22.85816574 W
PL12W           0.75169456 W
PL13W           0.22858167 W
SFO2           500.1322696 MHz

F2 - Processing parameters
SI                   65536
SF             125.7577699 MHz
WDW                     EM
SSB       0
LB                    3.00 Hz
GB        0
PC                    0.75
```

Figure S7. ^{13}C NMR spectrum of DTS(IIThTh$_{HEX}$)$_2$ in CDCl$_3$

Materials Characterization



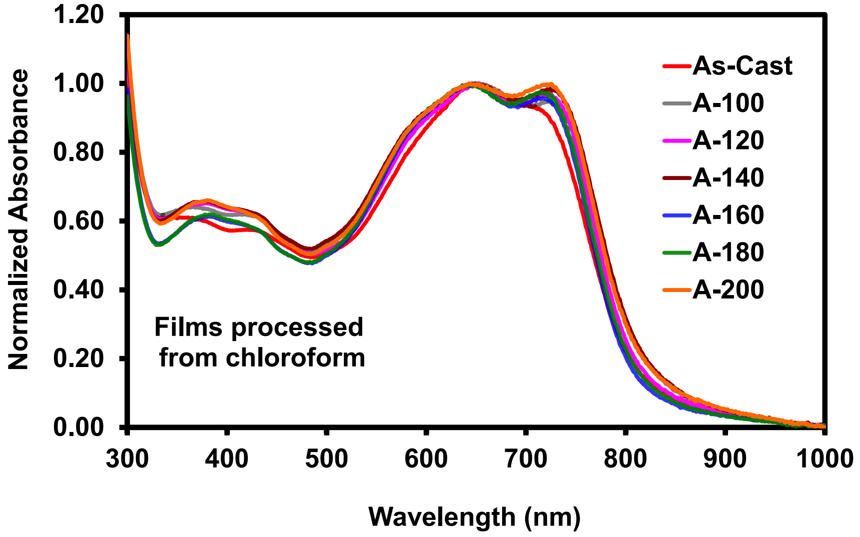


Figure S8. UV-vis specra for DTS(IIThTh$_{\mathrm{HEX}}$)$_2$ films processed from o-xylenes (TOP) and chloroform (BOTTOM). Films were annealed sequentially for 5 minutes at each temperature.

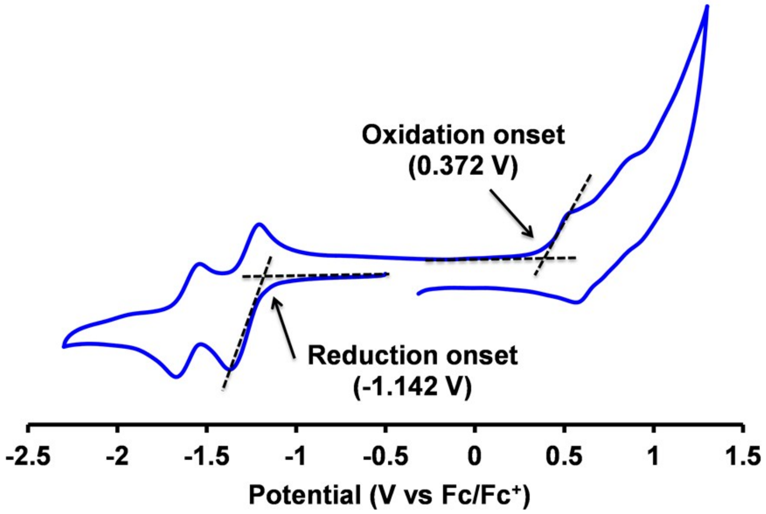


Figure S9. CV plot for DTS(IIThTh$_{HEX}$)$_2$ obtained in CH_2Cl_2 solution using ferrocene as the reference

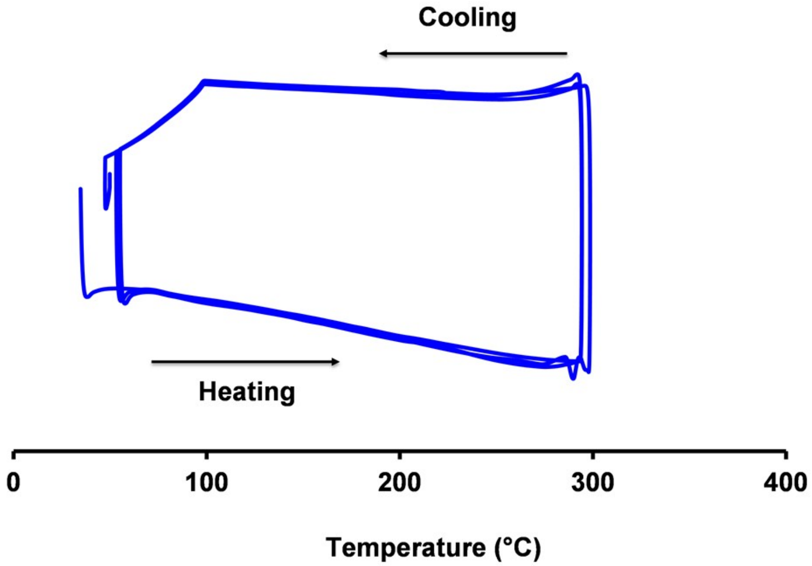
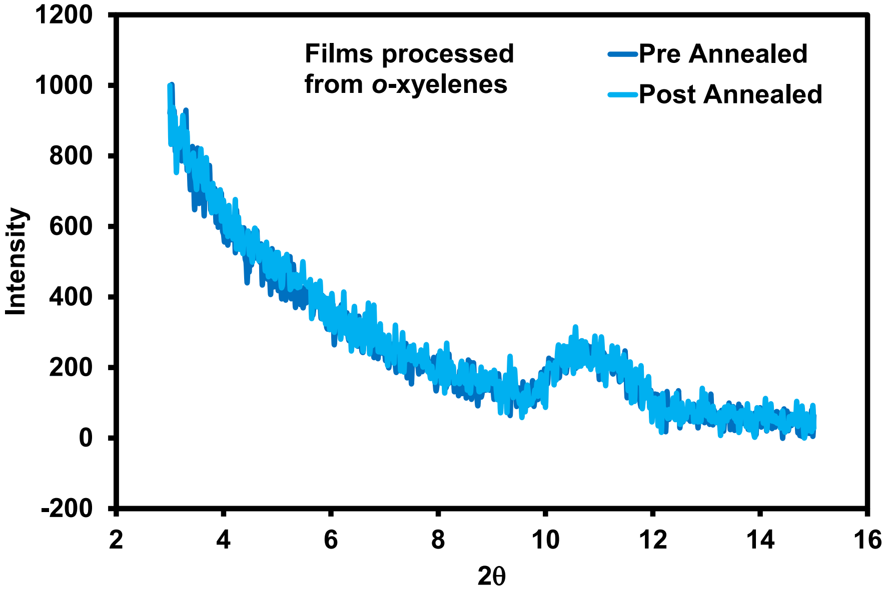


Figure S10. DSC plot for DTS(IIThTh$_{HEX}$)$_2$. Scan rate of 10°C/s



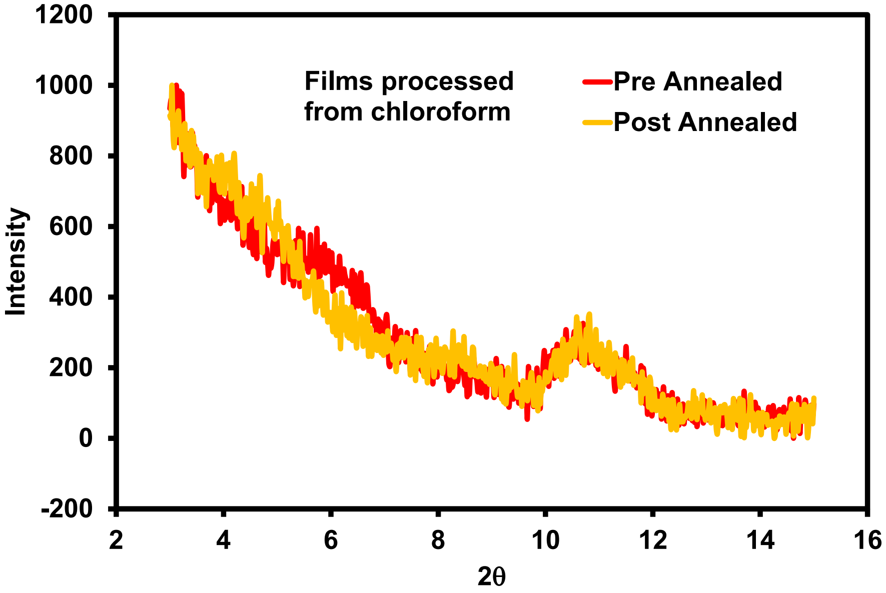


Figure S11. XRD plots for thin-films of DTS(IIThTh$_{HEX}$)$_2$. Films were spin-cast from 15 mg/mL solutions of o-xylenes (TOP, blue) or chloroform (BOTTOM, red) at 1000 rpm onto glass substrates. Films were subject to analysis as-cast and after thermal annealing (100 °C), no significant diffraction peaks were observed.

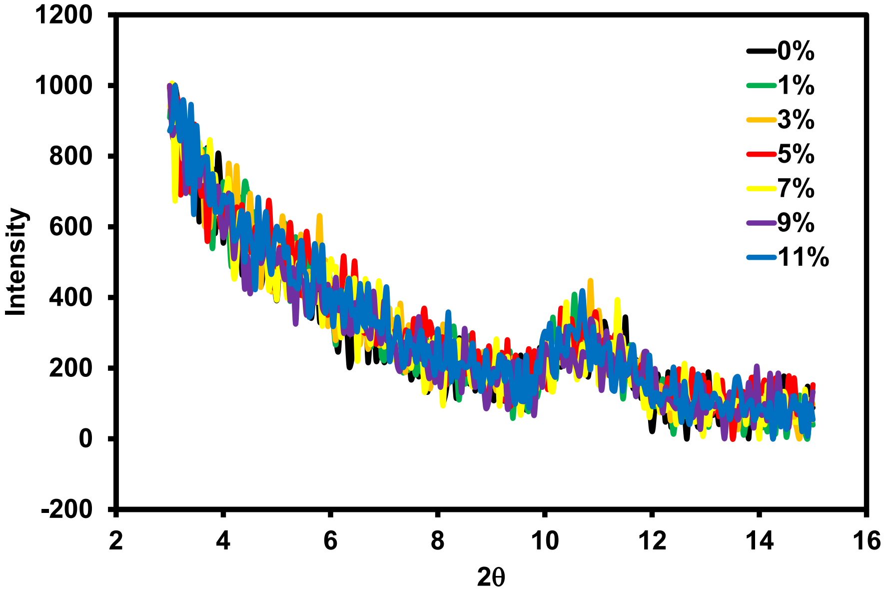


Figure S12. XRD plots for thin-films of DTS(IIThTh$_{HEX}$)$_2$:PC$_{61}$BM. Films were spin-cast from 30 mg/mL (50:50 D:A ratio) solutions of chloroform with DIO added (v/v%) at 1500 rpm onto PEDOT:PSS coated glass substrates. No significant diffraction peaks were observed.

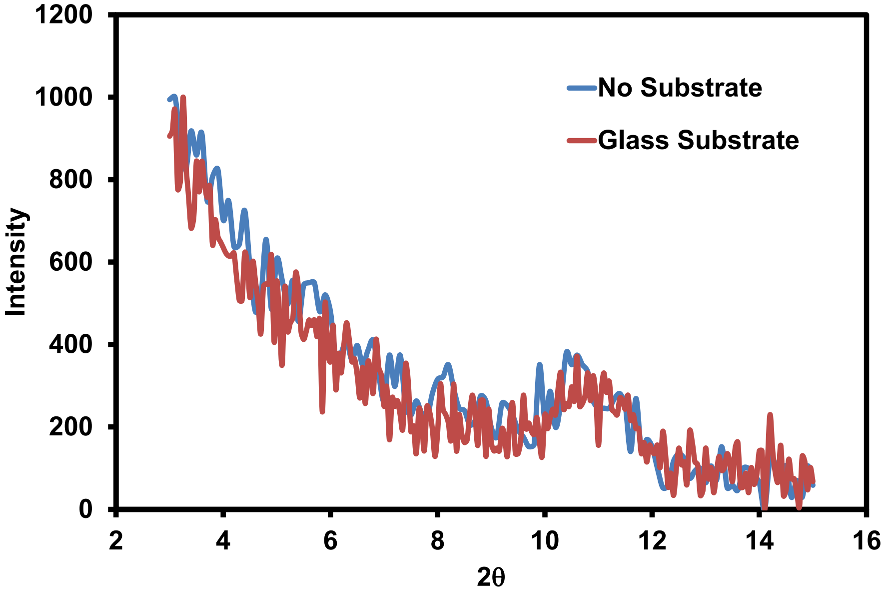
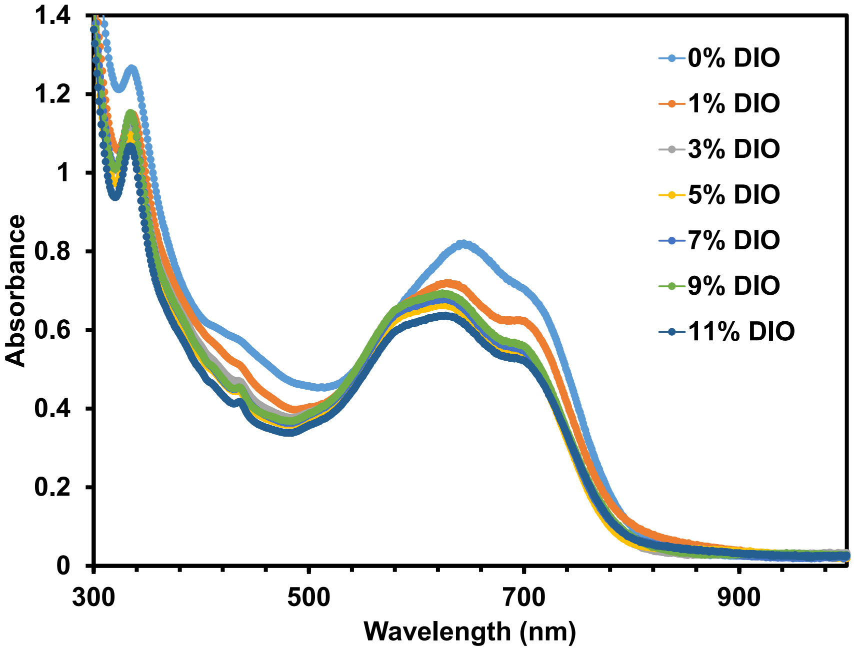


Figure S13. XRD plots from scans run with no substrate and a glass substrate. The broad hump from 10-12 θ is an artifact of the experiment and is not due to the sample.



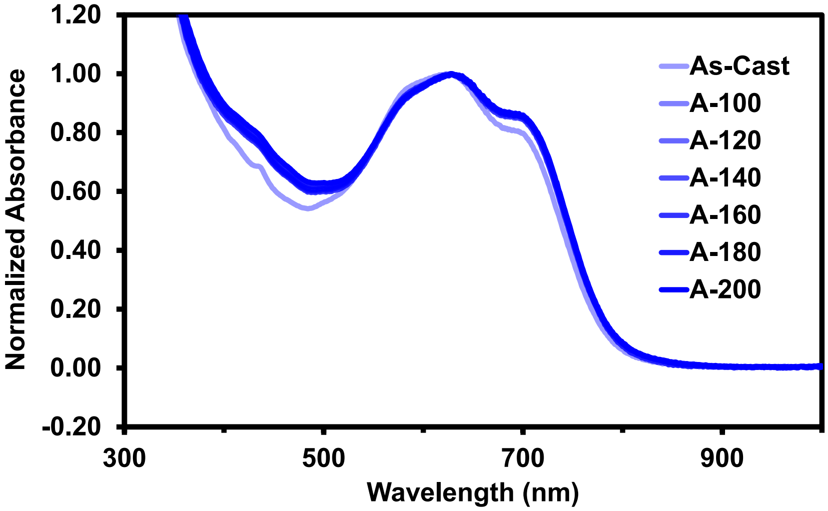


Figure S14. UV-vis spectra for DTS(IIThTh$_{\mathrm{HEX}}$)$_2$**:**PC$_6$1BM films (50:50) processed from CHCl$_3$ with varying amounts of DIO additive (v/v) (Top). UV-vis spectra for DTS(IIThTh$_{\mathrm{HEX}}$)$_2$**:**PC$_6$1BM films (50:50) processed from CHCl$_3$ with 5% v/v DIO additive as-cast and thermally annealed at various temperatures (Bottom).

Theoretical Calculations

Table S1. Calculated electronic transitions for DTS(IIThTh$_{HEX}$)$_2$ using TD-DFT methods.

State	**E_{opt} (eV)**	**λ (nm)**	**f**	**Composition**
S_1	1.73	718	2.562	HOMO → LUMO (96%)
S_2	1.98	626	0.166	HOMO → LUMO +1 (97%)
S_3	2.06	602	0.241	HOMO -1 → LUMO (92%)
S_4	2.21	562	0.154	HOMO -1 → LUMO +1 (59%)
S_9	2.56	485	0.184	HOMO -4 → LUMO (40%)
S_{12}	2.87	433	0.309	HOMO → LUMO+2 (84%)

Solar Cell Device Characterization

Table S2. V_{OC}, J_{SC}, FF and PCE of **DTS(IIThTh$_{HEX}$)$_2$**/PC$_{61}$BM devices. Active layer films were cast from o-xylenes or chloroform (3% wt/v total solids). Devices were measure as-cast and after thermal annealing. Devices were annealed post cathode deposition sequentially from 100-180°C at 10°C intervals for 5 minutes under N_2. Only best performance devices are reported.

Description and Condition	**V_{OC} (V)**	**J_{SC} (mA cm^{-2})**	**FF**	**PCE (%)**
o-xylene, 70:30, as-cast[1]	**0.539 ± 0.03**	**1.07 ± 0.01**	**0.35 ± 0.03**	**0.17 ± 0.02**
o-xylene, 60:40, as-cast[1]	**0.483 ± 0.04**	**1.15 ± 0.04**	**0.36 ± 0.04**	**0.16 ± 0.01**
o-xylene, 50:50, as-cast[1]	**0.351 ± 0.09**	**1.05 ± 0.07**	**0.40 ± 0.06**	**0.12 ± 0.04**
o-xylene, 40:60, as-cast[1]	**0.327 ± 0.2**	**1.31 ± 0.01**	**0.49 ± 0.04**	**0.16 ± 0.1**
o-xylene, 30:70, as-cast[1]	**0.605 ± 0.01**	**1.38 ± 0.01**	**0.48 ± 0.05**	**0.38 ± 0.01**
CHCl$_3$, 70:30, A-180[2]	**0.672 ± 0.003**	**1.48 ± 0.01**	**0.36 ± 0.005**	**0.36 ± 0.005**
CHCl$_3$, 60:40, A-180[2]	**0.705 ± 0.01**	**4.31 ± 0.08**	**0.37 ± 0.005**	**1.13 ± 0.007**
CHCl$_3$, 50:50, A-180[2]*	**0.730 ± 0.03**	**4.06 ± 0.07**	**0.45 ± 0.02**	**1.33 ± 0.2**
CHCl$_3$, 40:60, A-160[2]	**0.712 ± 0.004**	**3.98 ± 0.1**	**0.46 ± 0.005**	**1.30 ± 0.03**
CHCl$_3$, 30:70, A-160[2]	**0.700 ± 0.02**	**3.76 ± 0.1**	**0.41 ± 0.02**	**1.07 ± 0.05**
CHCl$_3$, 50:50, as-cast[2]	**0.703 ± 0.07**	**2.51 ± 0.1**	**0.45 ± 0.07**	**0.82 ± 0.2**
CHCl$_3$, 50:50, A-100[2]	**0.719 ± 0.04**	**2.62 ± 0.1**	**0.46 ± 0.04**	**0.87 ± 0.1**
CHCl$_3$, 50:50, A-140[2]	**0.734 ± 0.02**	**3.22 ± 0.1**	**0.47 ± 0.02**	**1.11 ± 0.07**
CHCl$_3$, 50:50, A-160[2]	**0.739 ± 0.02**	**3.76 ± 0.1**	**0.47 ± 0.02**	**1.30 ± 0.1**
CHCl$_3$, 50:50, A-180[2]*	**0.730 ± 0.03**	**4.06 ± 0.07**	**0.45 ± 0.02**	**1.33 ± 0.2**

[1] All devices spin-cast from xylenes showed best PCE without thermal annealing.
[2] All devices spin-cast from chloroform showed best PCE after thermal annealing for 5 minutes at 160 or 180°C.
[3] Results for 50:50 D:A base devices (spin-cast from chloroform) reported to show increase in PCE upon thermal annealing film (post-cathode deposition) sequential for 5 minutes at each temperature.
* Same data. Duplicated in table for consistency.

References

---

[1] J. Mei, K. R. Graham, R. Stalder, J. R. Reynold*, Org. Lett.* **2010**, *12*, 660-663.

[2] Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan, A. J. Heeger, *Nat. Mater.*, **2012**, *11*, 44–48.