Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information (ESI)

Transition-metal-free and halogen-free controlled synthesis of poly(3-alkylthienylene vinylene) via Horner-Wadsworth-Emmons condensation reaction

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Materials

Tetrahydrofuran, stabilizer free (THF, 99.5%, Kanto Chemical Co., Inc.) was refluxed over sodium benzophenone under nitrogen for 2 h, then distilled just before use. 3-(2-Ethylhexyl)thiophene was synthesized according a previously reported procedure.[1] All other reagents were purchased from Sigma-Aldrich Japan K.K., Tokyo Chemical Industry Co., Ltd., Kanto Chemical Co., Inc. or Wako Pure Chemical Industries, Ltd., and used as received.

Measurement and characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECX400 in chloroform-*d* at 25 °C or 40 ºC calibrated to chloroform as a standard (δ_H 7.26). M_n and M_w/M_n were measured by size exclusion chromatography (SEC) on a Jasco GULLIVER 1500 equipped with an absorbance detector (UV, λ = 254 nm), and three polystyrene gel columns based on a conventional calibration curve using eight polystyrene standards. THF (40 °C) was used as a carrier solvent at a flow rate of 1.0 mL/min.

For Grazing-incidence wide-angle x-ray scattering (GIWAXS), P3EHTV was first dissolved in chloroform (4 mg/0.2 mL), followed by filtering through 0.45 μm pore size PTFE membrane syringe filters, and then spin-casted onto Si wafers.

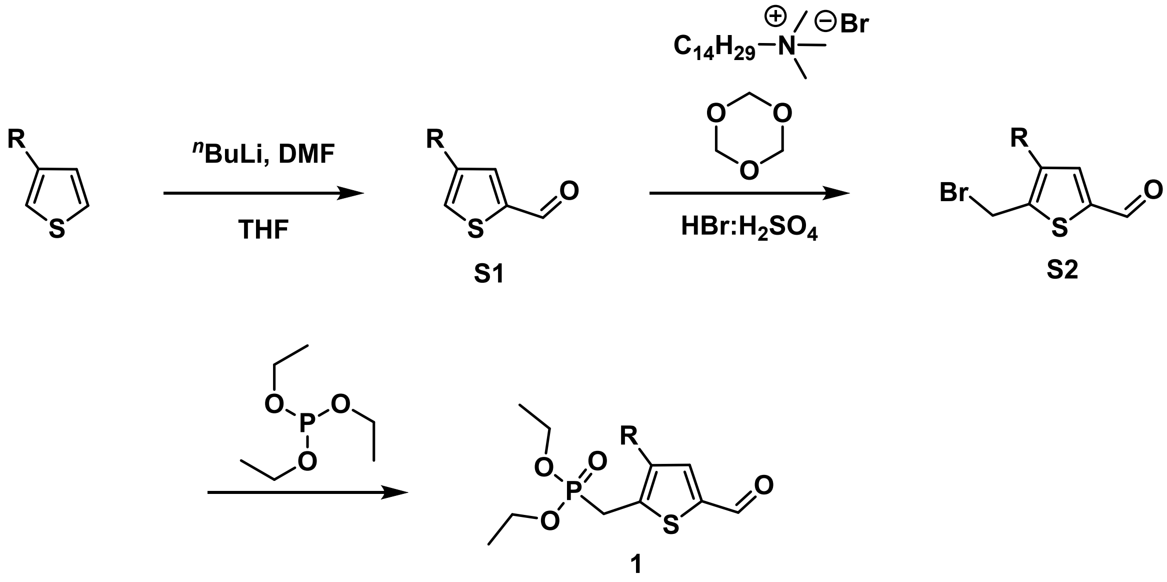
Measurements were conducted at the beamline BL46XU of SPring-8, Japan (proposal No. 2017B1744). The sample was irradiated at a fixed incident angle α_i on the order of 0.12° through a Huber diffractometer with an X-ray energy of 12.398 keV (X-ray wavelength λ = 0.10002 nm), and the GIWAXS patterns were recorded with a 2D image detector (Pilatus 300K) with the sample-to-detector distances of 172.5 mm. The scattering vectors q_y and q_z for GIWAXS are defined in Equation (1).

$$(q_y, q_z) = (2\pi (\sin \psi \cos \alpha_f) / \lambda, 2\pi (\sin \alpha_f + \sin \alpha_i) / \lambda) \qquad (1)$$

where ψ is out-of-plane angle, α_f is exit angle.

Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry analysis (TGA) and a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC). The UV−vis spectra were recorded by a JASCO V-670 spectrophotometer. For the solid state spectra, polymers were first dissolved in chloroform (~ 1 mg/mL) and then drop-casted onto quartz substrate. The polymer films were then thermally annealed at 150 °C for 1 h under vacuum.

Synthesis



R = (a) 2-ethylhexyl, (b) dodecyl

Scheme S1. Synthesis of monomer precursor (**1**)

Synthesis of 3-(2-ethylhexyl)-5-thiophenecarboxyaldehyde (S1a)

3-(2-Ethylhexyl)thiophene (4.91 g, 25.0 mmol) was placed in a 200 mL two-necked flask purged with N_2. After dissolving in anhydrous THF (100 mL), the solution was cooled down to -78 ºC. A 2.65 M hexane solution of ^{n}BuLi (9.4 mL, 25 mmol) was added slowly dropwise. The reaction mixture was stirred at -78 ºC for 30 min, then at room temperature for 1 h and the color changed from transparent to pale brown. Anhydrous *N,N*-dimethylformamide (2.5 mL, 32 mmol) was added dropwise at -78 ºC and stirred at room temperature for 2 h, followed by quenching with 5 M HCl aq. (5 mL) at 0 ºC. The quenched solution was extracted with Et_2O and washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, rotary evaporated and purified by silica gel chromatography using hexane/ethylacetate (19/1) as eluent to afford **S1a** (containing 6% of 3-(2-ethylhexyl)-2-thiophenecarboxyaldehyde (**S1a'**) which was removed in the next stage) as a pale yellow oil (5.40 g, 96%).

^{1}H NMR (400 MHz, chloroform-*d*): δ 10.0 (s, **S1a'**), 9.85 (s, 1H, **S1a**), 7.61 (d, *J* = 5.2 Hz, **S1a'**), 7.56 (s, 1H, **S1a**), 7.32 (s, 1H, **S1a**), 6.96 (d, *J* = 4.8 Hz, **S1a'**), 2.85 (d, *J* = 7.2 Hz, **S1a'**), 2.55 (d, *J* = 6.8 Hz, 2H, **S1a**), 1.68-1.47 (m, 1H), 1.35-1.14 (m, 8H), 0.92-0.79 (m, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 183.07 (**S1a**), 182.42 (**S1a'**), 152.24 (**S1a'**), 143.56 (**S1a**), 143.49 (**S1a**), 138.34 (**S1a'**), 137.78 (**S1a**), 134.28 (**S1a'**), 131.30, 41.60 (**S1a'**), 40.38 (**S1a**), 34.15, 32.74 (**S1a'**), 32.73(**S1a**), 28.87, 25.70 (**S1a'**), 25.51 (**S1a**), 23.03, 14.17, 10.84. Anal. Calcd. for $C_{13}H_{20}OS$ (%): C, 69.59; H, 8.99; S. 14.29. Found (%): C, 69.69; H, 9.65; S. 14.16.

Synthesis of 3-dodecyl-5-thiophenecarboxyaldehyde (S1b)

3-Dodecylthiophene (4.46 g, 17.7 mmol) was reacted and purified by following the same procedure as described for **S1a**. **S1b** was obtained as a pale yellow oil (4.47 g, 90%) (containing 12% of 3-dodecyl-2-thiophenecarboxyaldehyde (**S1b'**) which was removed in the next stage).

^{1}H NMR (400 MHz, chloroform-*d*): δ 10.0 (s, **S1b'**), 9.87 (s, 1H, **S1b**), 7.64 (d, *J* = 5.2 Hz, **S1b'**), 7.61 (s, 1H, **S1b**), 7.37 (s, 1H, **S1b**), 7.01 (d, *J* = 5.2 Hz, **S1b'**), 2.96 (t, *J* = 7.8 Hz, **S1b'**), 2.63 (t, *J* = 7.8 Hz, 2H, **S1b**), 1.71-1.54 (m, 2H), 1.39-1.16 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 183.25 (**S1b**), 182.51 (**S1b'**), 153.16 (**S1b'**), 144.91 (**S1b**), 143.67 (**S1b**), 137.41, 134.62 (**S1b'**), 130.84 (**S1b'**), 130.62 (**S1b**), 32.06, 30.54, 30.26, 29.78, 29.69, 29.54, 29.50, 29.29, 22.84, 14.29. Anal. Calcd. for $C_{17}H_{28}OS$ (%): C, 72.80; H, 10.06; S. 11.43. Found (%): C, 72.74; H, 10.02; S. 11.73.

Synthesis of 3-(2-ethylhexyl)-2-bromomethyl-5-thiophenecarboxy aldehyde (S2a)

S1a (5.27 g, 23.5 mmol) and hydrobromic acid (47 wt% in water) 100 mL were placed in a 200 mL two-necked flask with condenser and glass plug purged with N_2. After the mixture was cooled down to 0 °C, sulfulic acid (conc.) 33 mL, trioxane (2.32 g, 25.8 mmol) and tetradecyltrimethylammonium bromide (0.791 g, 2.35 mmol) were added and stirred at 60 ºC for 5 h. Then, the reaction mixture was poured into 300 mL of water. The solution was extracted with chloroform, washed with water and brine. The organic phase was dried over anhydrous magnesium sulfate, rotary evaporated and purified by silica gel chromatography using hexane/ethylacetate (9/1) as eluent to afford **S2a** as a dark yellow oil (6.19 g, 83%).

^{1}H NMR (400 MHz, chloroform-*d*): δ 9.85 (s, 1H), 7.49 (s, 1H), 4.65 (s, 1H), 2.54 (d, *J* = 6.8 Hz, 2H), 1.68-1.57 (m, 1H), 1.40-1.17 (m, 8H), 0.94-0.84 (m, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 183.01, 144.35, 142.91, 142.12, 138.19, 40.33, 32.73, 28.96, 25.88, 24.13, 23.11, 14.23, 10.98. Anal. Calcd. for $C_{14}H_{21}BrOS$ (%): C, 53.00; H, 6.67; S. 10.10. Found (%): C, 53.26; H, 6.79; S. 9.93.

Synthesis of 3-dodecyl-2-bromomethyl-5-thiophenecarboxy aldehyde (S2b)

S1b (3.95 g, 14.1 mmol) was reacted and purified by following the same procedure as described for **S2a**. **S2b** was obtained as a white solid (3.92 g, 75%).

^{1}H NMR (400 MHz, chloroform-*d*): δ 9.84 (s, 1H), 7.53 (s, 1H), 4.64 (s, 1H), 2.61 (t, *J* = 8.0 Hz, 2H), 1.71-1.58 (m, 2H), 1.45-1.14 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 182.98, 143.85, 143.71, 142.25, 137.72, 32.07, 30.08, 29.78, 29.67, 29.56, 29.53, 29.49, 28.34, 24.01, 22.84, 14.27. Anal. Calcd. for $C_{18}H_{29}BrOS$ (%): C, 57.90; H, 7.83; S. 8.59. Found (%): C, 58.04; H, 7.70; S. 8.43.

Synthesis of (3-(2-ethylhexyl)-5-formyl-thiophene-2-ylmethyl)phosphonic acid diethyl ester (1a)

S2a (4.65 g, 14.7 mmol) and triethylphosphite (7.31 g, 44.0 mmol) were placed in a 20 mL one-necked flask purged with N_2. The solution was stirred at 100 °C for 3 h. After cooling down to room temperature, excess triethylphosphite was removed by a vacuum pump. The resulting crude dark red oil was purified by silica gel chromatography for three times using hexane/ethylacetate (4/6) as eluent to afford **1a** as a viscous reddish yellow oil (3.52 g, 64%).

^{1}H NMR (400 MHz, chloroform-*d*): δ 9.76 (d, *J* = 1.6 Hz, 1H), 7.46 (s, 1H), 4.14-3.95 (m, 4H), 3.30 (d, *J* = 22.0 Hz, 2H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.60-1.42 (m, 1H), 1.40-1.05 (m, 8H), 0.94-0.70 (m, 6H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 182.77, 141.88 (d, *J* =8.7 Hz), 141.07 (d, *J* =3.8 Hz), 138.81 (d, *J* = 11.6 Hz), 138.34 (d, *J* = 3.8 Hz), 62.73 (d, *J* = 6.8 Hz), 40.46, 32.61, 28.99, 28.29, 26.85, 25.73, 23.12, 16.55, 16.49, 14.21, 10.96. Anal. Calcd. for $C_{18}H_{31}O_4PS$ (%): C, 57.73; H, 8.34; S. 8.56. Found (%): C, 57.45; H, 8.58; S. 8.94.

Synthesis of (3-dodecyl-5-formyl-thiophene-2-ylmethyl)phosphonic acid diethyl ester (1b)

S2b (3.43 g, 9.19 mmol) was reacted and purified by following the same procedure as described for **1a**. **1b** was obtained as viscous reddish yellow oil (3.15 g, 80%).

^{1}H NMR (400 MHz, chloroform-*d*): δ 9.80 (d, *J* = 1.6 Hz, 1H), 7.53 (s, 1H), 4.18-3.99 (m, 4H), 3.33 (d, *J* = 22.0 Hz, 2H), 2.63-2.55 (m, 2H), 1.65-1.53 (m, 2H), 1.41-1.15 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 182.73, 142.77 (d, *J* =8.7 Hz), 141.26 (d, *J* = 2.8 Hz), 138.25 (d, *J* = 11.6 Hz), 137.79 (d, *J* = 3.8 Hz), 62.77 (d, *J* = 6.8 Hz), 32.05, 30.30, 29.77, 29.70, 29.61, 29.57, 29.48, 28.35, 28.25, 26.81, 22.82, 16.56, 16.50, 14.25. Anal. Calcd. for $C_{22}H_{39}O_4PS$ (%): C, 61.37; H, 9.13; S. 7.45. Found (%): C, 61.06; H, 9.70; S. 7.27.

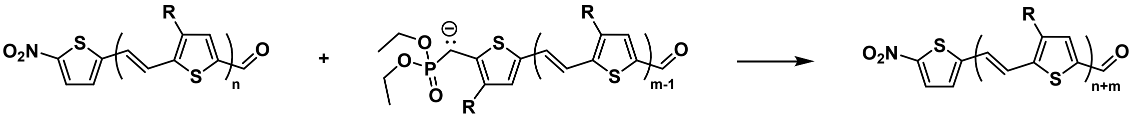
Post-polymerization of 1a for P3EHTV

Anhydrous THF (18 mL), 15-crown-5-ether (0.10 mL, 0.51 mmol) and a 1.9 M THF solution of sodium hexamethyldisilazide (0.28 mL, 0.53 mmol) were placed in a 50 mL two-necked flask purged with N_2 and cooled down to -78 ºC. 2 mL **1a** solution which was prepared in another 5 mL two-necked flask with **1a** (186 mg, 0.497 mmol) and anhydrous THF (2 mL) was also cooled down to -78 ºC and immediately added to the reaction mixture. After stirring for 5 min, 5-nitro-2-thiophenecarboxaldehyde (6.5 mg, 0.041 mmol), which was dissolved in THF (0.5 mL), was added to start the polymerization. The polymerization was carried out at -40 °C for 30 min. After sampling an aliquot of the solution and quenching with 5 M HCl aq. for SEC characterization (M_n (SEC) = 4,200, M_w/M_n = 1.19), the 2nd monomer solution was added to the reaction mixture, which was prepared in another batch as described below. The solution was further stirred at -40 ºC for additional 2 h, followed by quenching with 5 M HCl aq. (2 mL). The quenched solution was extracted with chloroform, washed with water, and analyzed by SEC directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtering and drying under vacuum, the crude P3EHTV was obtained as a dark blue solid (206 mg, 94%). SEC: M_n = 6,900, M_w/M_n = 1.29.

Preparation of THF solution of the 2nd monomer

Anhydrous THF (8 mL), 15-crown-5-ether (0.10 mL, 0.51 mmol) and a 1.9 M THF solution of sodium hexamethyldisilazide (0.27 mL, 0.51 mmol) were placed in a 10 mL two-necked flask purged with N_2 and cooled down to -78 ºC. 2 mL **1a** solution which was prepared in another 5 mL two-necked flask with **1a** (186 mg, 0.497 mmol) and anhydrous THF (2 mL) was also cooled down to -78 ºC to afford the 2nd monomer solution.

Plausible mechanism for polymer coupling reaction between formyl-terminated P3EHTV and phosphonic-acid-ester-terminated P3EHTV.



Scheme S2. Polymer coupling reaction between formyl-terminated P3EHTV and phosphonic-acid-ester-terminated P3EHTV

^{1}H and ^{13}C NMR spectra

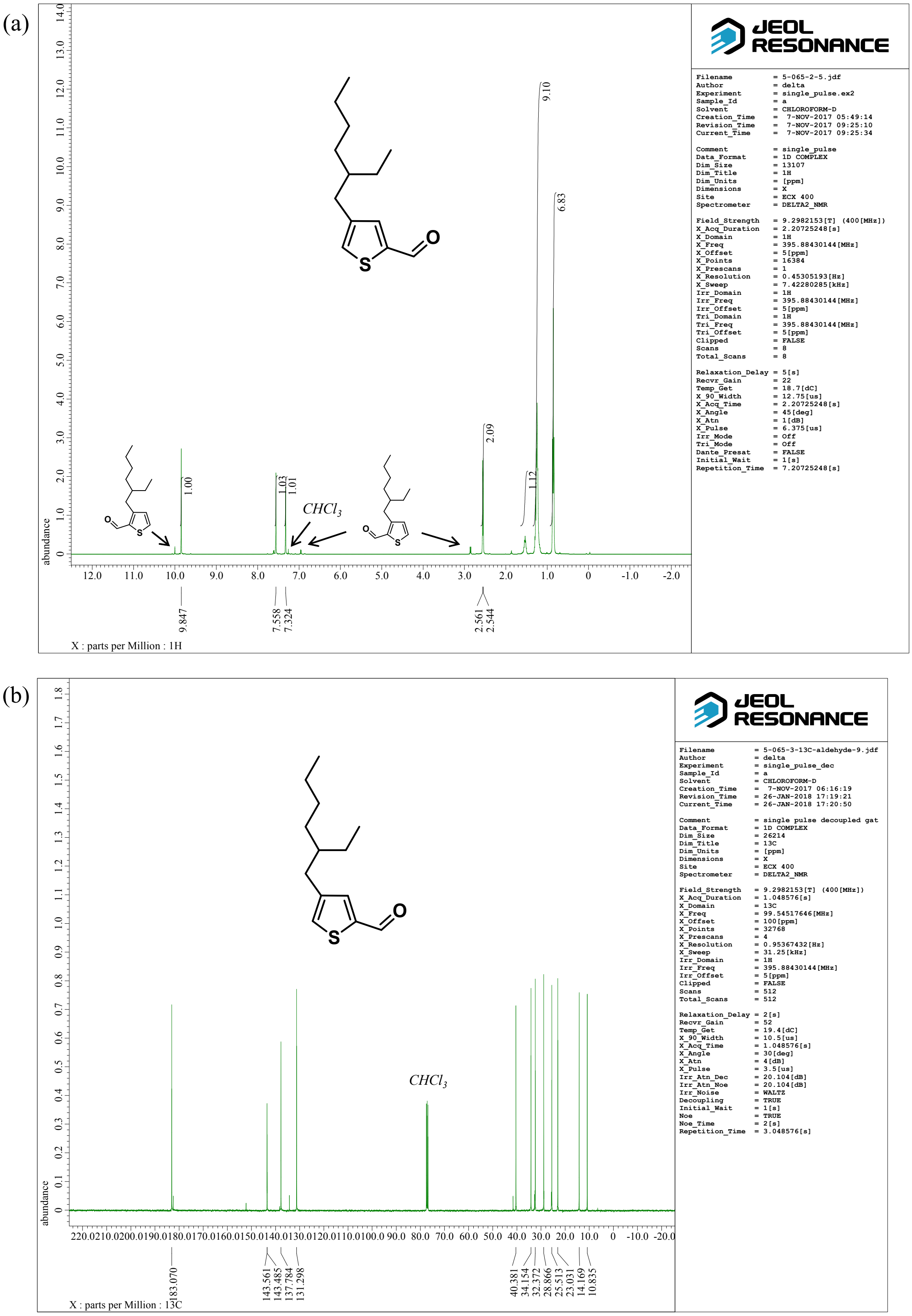


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Figure S1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **S1a**.

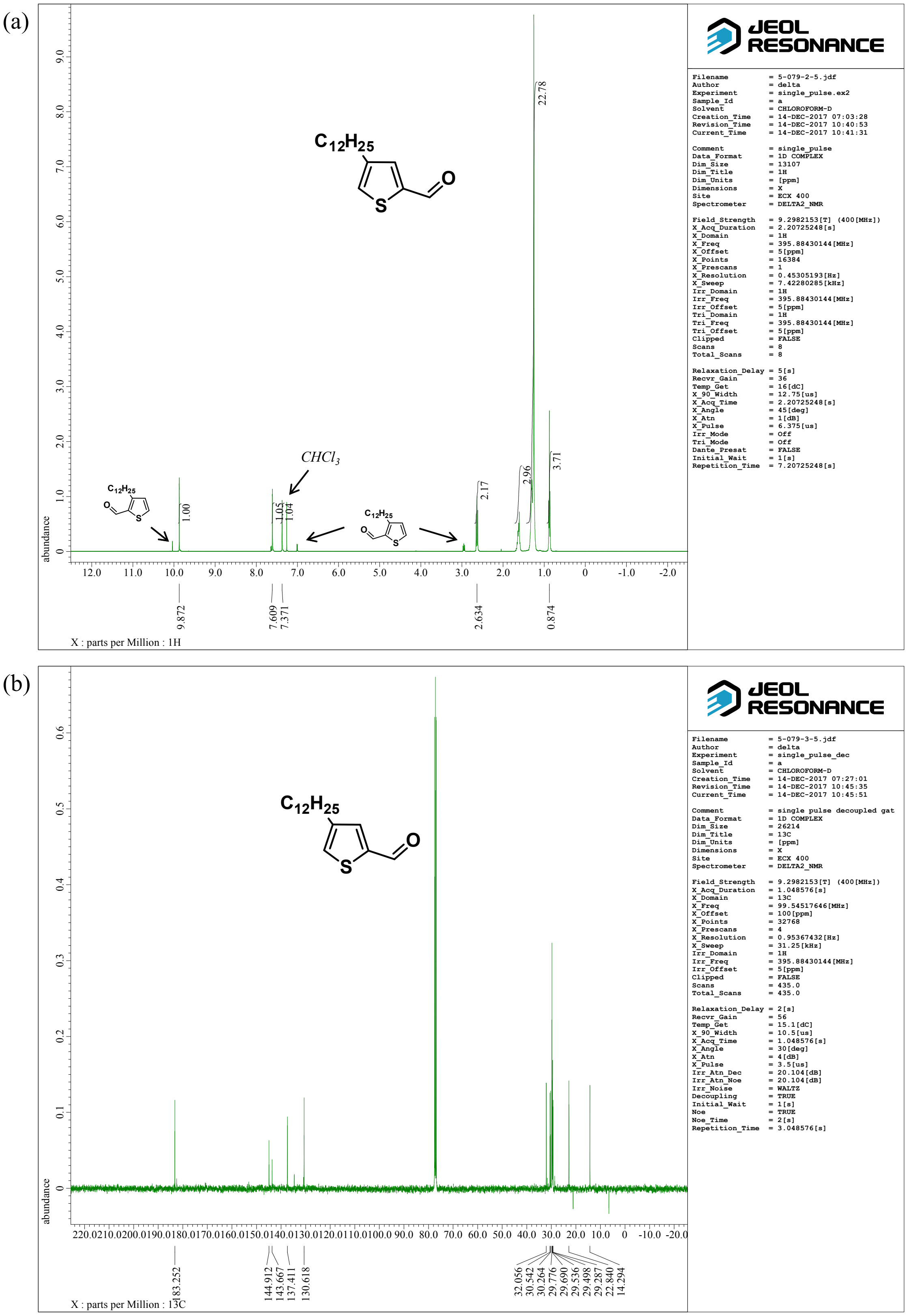

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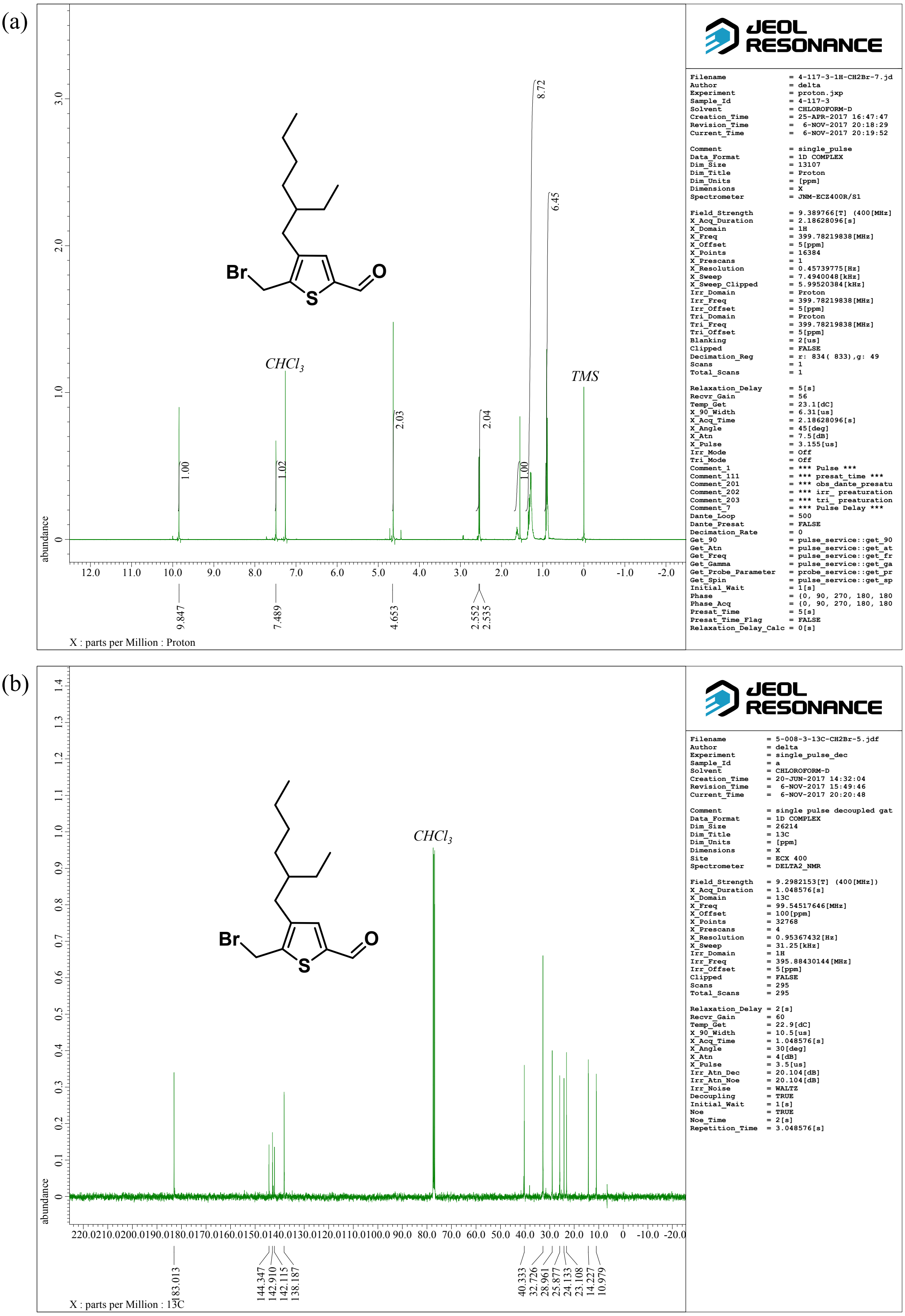
Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **S1b**.



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Decimation_Rate       = 0
Get_90                = pulse_service::get_90
Get_Atn               = pulse_service::get_at
Get_Freq              = pulse_service::get_fr
Get_Gamma             = pulse_service::get_ga
Get_Probe_Parameter   = probe_service::get_pr
Get_Spin              = pulse_service::get_sp
Initial_Wait          = 1[s]
Phase                 = {0, 90, 270, 180, 180
Phase_Acq             = {0, 90, 270, 180, 180
Presat_Time           = 5[s]
Presat_Time_Flag      = FALSE
Relaxation_Delay_Calc = 0[s]
```

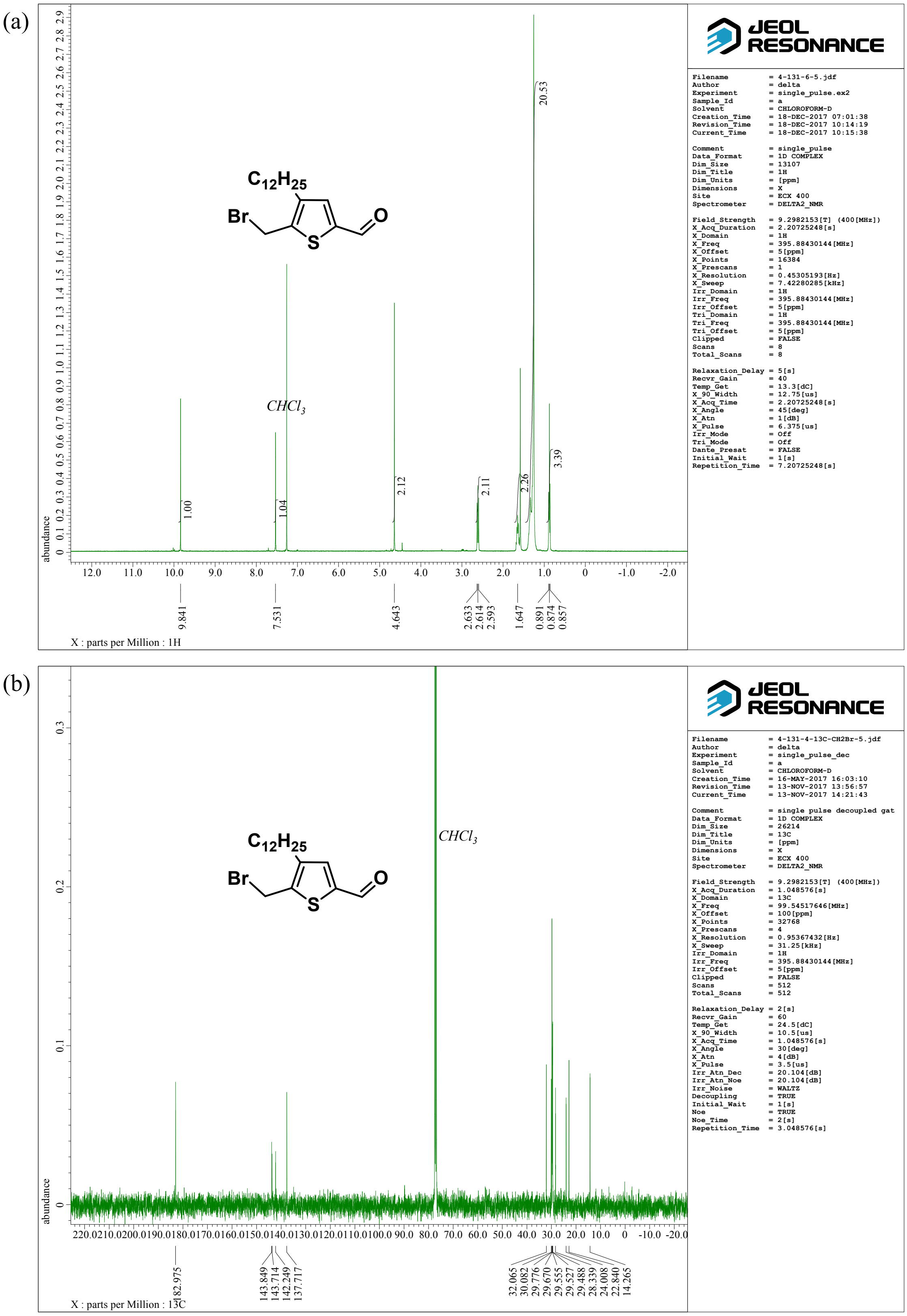
```
Filename         = 5-008-3-13C-CH2Br-5.jdf
Author           = delta
Experiment       = single_pulse_dec
Sample_Id        = a
Solvent          = CHLOROFORM-D
Creation_Time    = 20-JUN-2017 14:32:04
Revision_Time    =  6-NOV-2017 15:49:46
Current_Time     =  6-NOV-2017 20:20:48

Comment          = single pulse decoupled gat
Data_Format      = 1D COMPLEX
Dim_Size         = 26214
Dim_Title        = 13C
Dim_Units        = [ppm]
Dimensions       = X
Site             = ECX 400
Spectrometer     = DELTA2_NMR

Field_Strength   = 9.2982153[T] (400[MHz])
X_Acq_Duration   = 1.048576[s]
X_Domain         = 13C
X_Freq           = 99.54517646[MHz]
X_Offset         = 100[ppm]
X_Points         = 32768
X_Prescans       = 4
X_Resolution     = 0.95367432[Hz]
X_Sweep          = 31.25[kHz]
Irr_Domain       = 1H
Irr_Freq         = 395.88430144[MHz]
Irr_Offset       = 5[ppm]
Clipped          = FALSE
Scans            = 295
Total_Scans      = 295

Relaxation_Delay = 2[s]
Recvr_Gain       = 60
Temp_Get         = 22.9[dC]
X_90_Width       = 10.5[us]
X_Acq_Time       = 1.048576[s]
X_Angle          = 30[deg]
X_Atn            = 4[dB]
X_Pulse          = 3.5[us]
Irr_Atn_Dec      = 20.104[dB]
Irr_Atn_Noe      = 20.104[dB]
Irr_Noise        = WALTZ
Decoupling       = TRUE
Initial_Wait     = 1[s]
Noe              = TRUE
Noe_Time         = 2[s]
Repetition_Time  = 3.048576[s]
```

Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **S2a**.



```
Filename          = 4-131-6-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 18-DEC-2017 07:01:38
Revision_Time     = 18-DEC-2017 10:14:19
Current_Time      = 18-DEC-2017 10:15:38

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 2.20725248[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45305193[Hz]
X_Sweep           = 7.42280285[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 40
Temp_Get          = 13.3[dC]
X_90_Width        = 12.75[us]
X_Acq_Time        = 2.20725248[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.375[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.20725248[s]
```

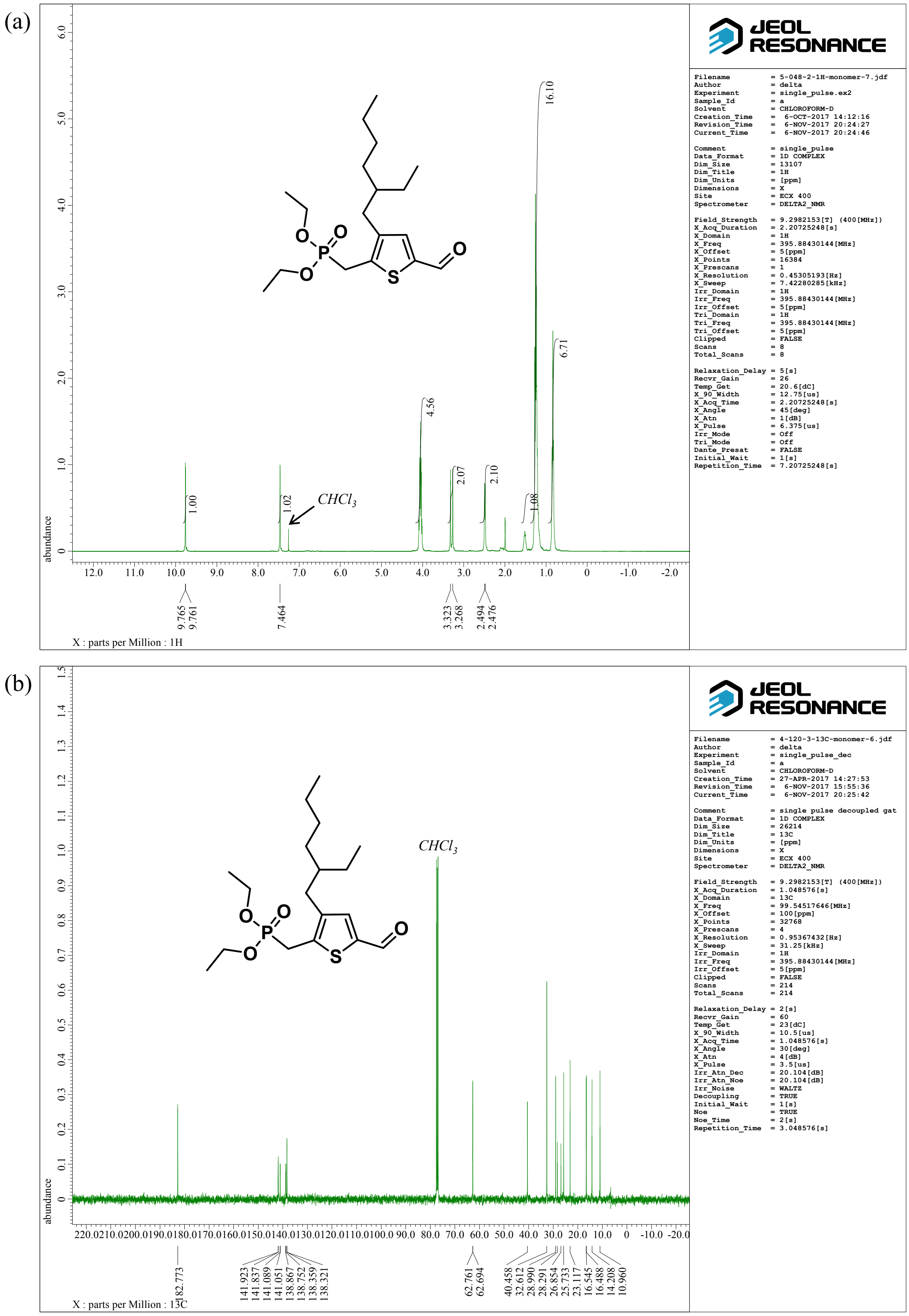
```
Filename          = 4-131-4-13C-CH2Br-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 16-MAY-2017 16:03:10
Revision_Time     = 13-NOV-2017 13:56:57
Current_Time      = 13-NOV-2017 14:21:43

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 1.048576[s]
X_Domain          = 13C
X_Freq            = 99.54517646[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95367432[Hz]
X_Sweep           = 31.25[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 24.5[dC]
X_90_Width        = 10.5[us]
X_Acq_Time        = 1.048576[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.5[us]
Irr_Atn_Dec       = 20.104[dB]
Irr_Atn_Noe       = 20.104[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.048576[s]
```

Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **S2b**.



```
Filename          = 5-048-2-1H-monomer-7.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     =  6-OCT-2017 14:12:16
Revision_Time     =  6-NOV-2017 20:24:27
Current_Time      =  6-NOV-2017 20:24:46

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 2.20725248[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45305193[Hz]
X_Sweep           = 7.42280285[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 26
Temp_Get          = 20.6[dC]
X_90_Width        = 12.75[us]
X_Acq_Time        = 2.20725248[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.375[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.20725248[s]
```

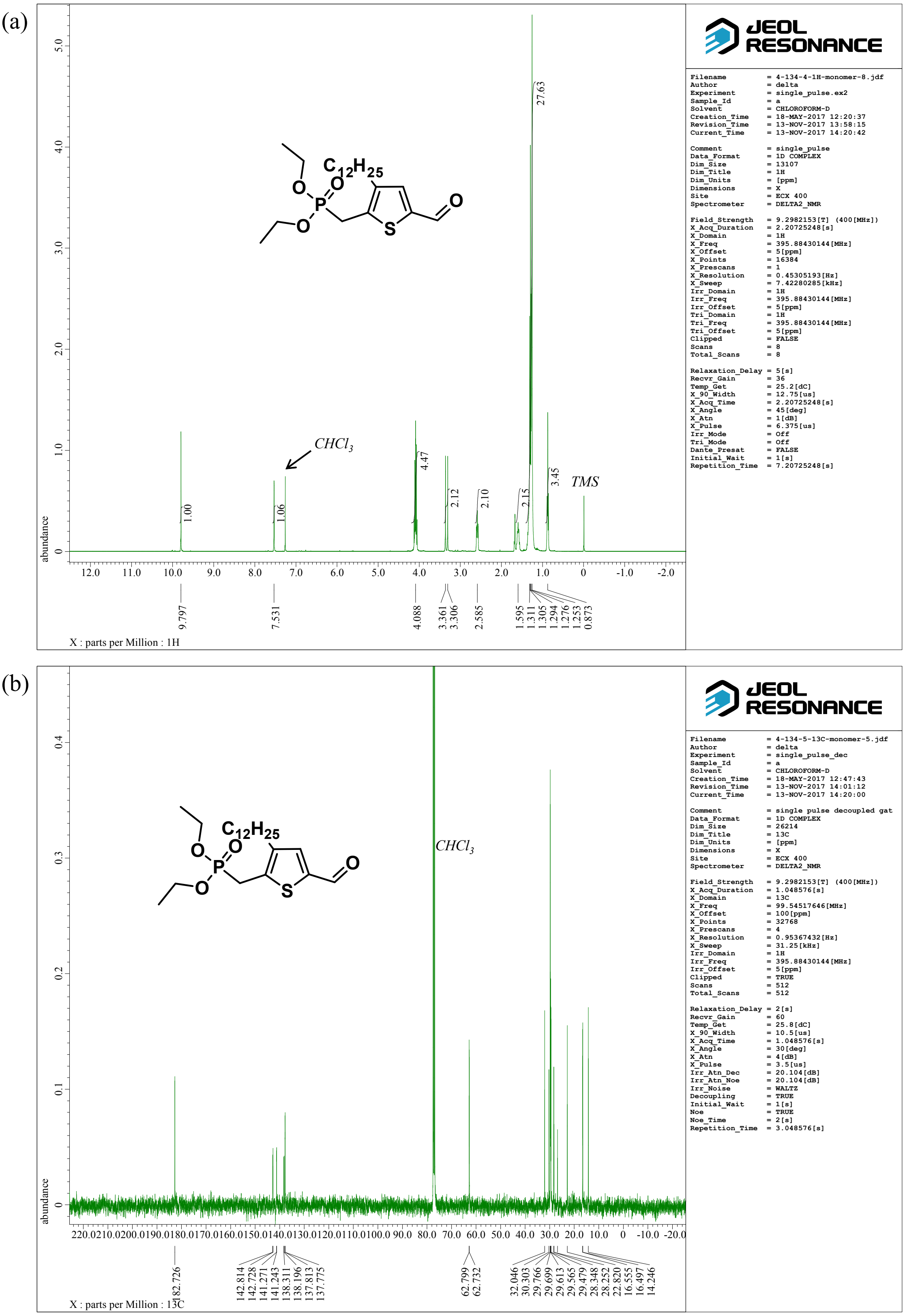
```
Filename          = 4-120-3-13C-monomer-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 27-APR-2017 14:27:53
Revision_Time     =  6-NOV-2017 15:55:36
Current_Time      =  6-NOV-2017 20:25:42

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 1.048576[s]
X_Domain          = 13C
X_Freq            = 99.54517646[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95367432[Hz]
X_Sweep           = 31.25[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 214
Total_Scans       = 214

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 23[dC]
X_90_Width        = 10.5[us]
X_Acq_Time        = 1.048576[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.5[us]
Irr_Atn_Dec       = 20.104[dB]
Irr_Atn_Noe       = 20.104[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.048576[s]
```

Figure S5. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **1a**.



```
Filename          = 4-134-4-1H-monomer-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 18-MAY-2017 12:20:37
Revision_Time     = 13-NOV-2017 13:58:15
Current_Time      = 13-NOV-2017 14:20:42

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 2.20725248[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45305193[Hz]
X_Sweep           = 7.42280285[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 8
Total_Scans       = 8

Relaxation_Delay = 5[s]
Recvr_Gain        = 36
Temp_Get          = 25.2[dC]
X_90_Width        = 12.75[us]
X_Acq_Time        = 2.20725248[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.375[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.20725248[s]
```

```
Filename          = 4-134-5-13C-monomer-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 18-MAY-2017 12:47:43
Revision_Time     = 13-NOV-2017 14:01:12
Current_Time      = 13-NOV-2017 14:20:00

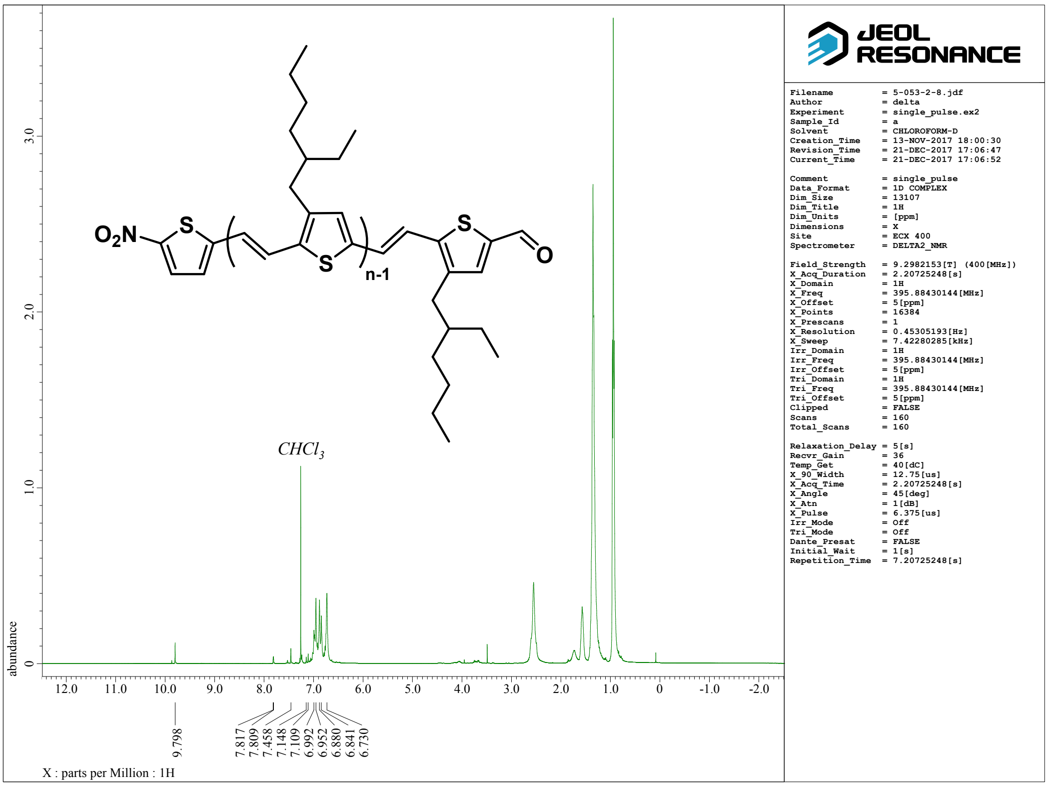
Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 1.048576[s]
X_Domain          = 13C
X_Freq            = 99.54517646[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95367432[Hz]
X_Sweep           = 31.25[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Clipped           = TRUE
Scans             = 512
Total_Scans       = 512

Relaxation_Delay = 2[s]
Recvr_Gain        = 60
Temp_Get          = 25.8[dC]
X_90_Width        = 10.5[us]
X_Acq_Time        = 1.048576[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.5[us]
Irr_Atn_Dec       = 20.104[dB]
Irr_Atn_Noe       = 20.104[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.048576[s]
```

Figure S6. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **1b**.

(a)



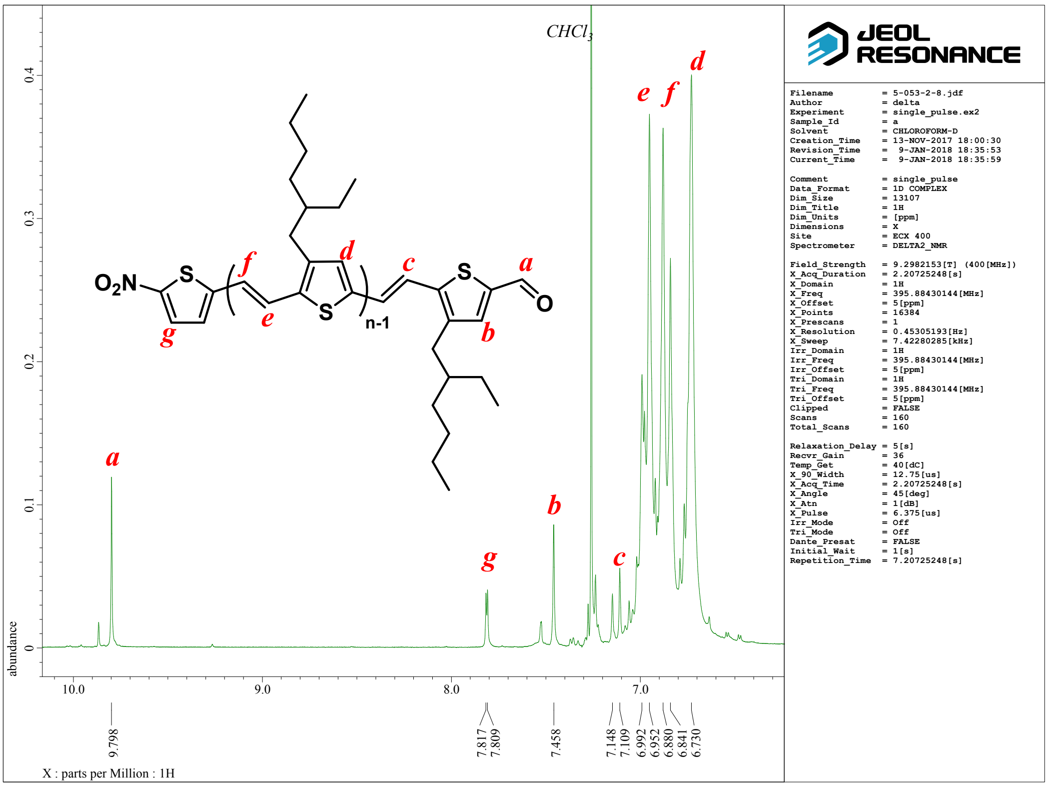
```
Filename          = 5-053-2-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 13-NOV-2017 18:00:30
Revision_Time     = 21-DEC-2017 17:06:47
Current_Time      = 21-DEC-2017 17:06:52

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 2.20725248[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45305193[Hz]
X_Sweep           = 7.42280285[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 160
Total_Scans       = 160

Relaxation_Delay = 5[s]
Recvr_Gain        = 36
Temp_Get          = 40[dC]
X_90_Width        = 12.75[us]
X_Acq_Time        = 2.20725248[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.375[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.20725248[s]
```

(b)



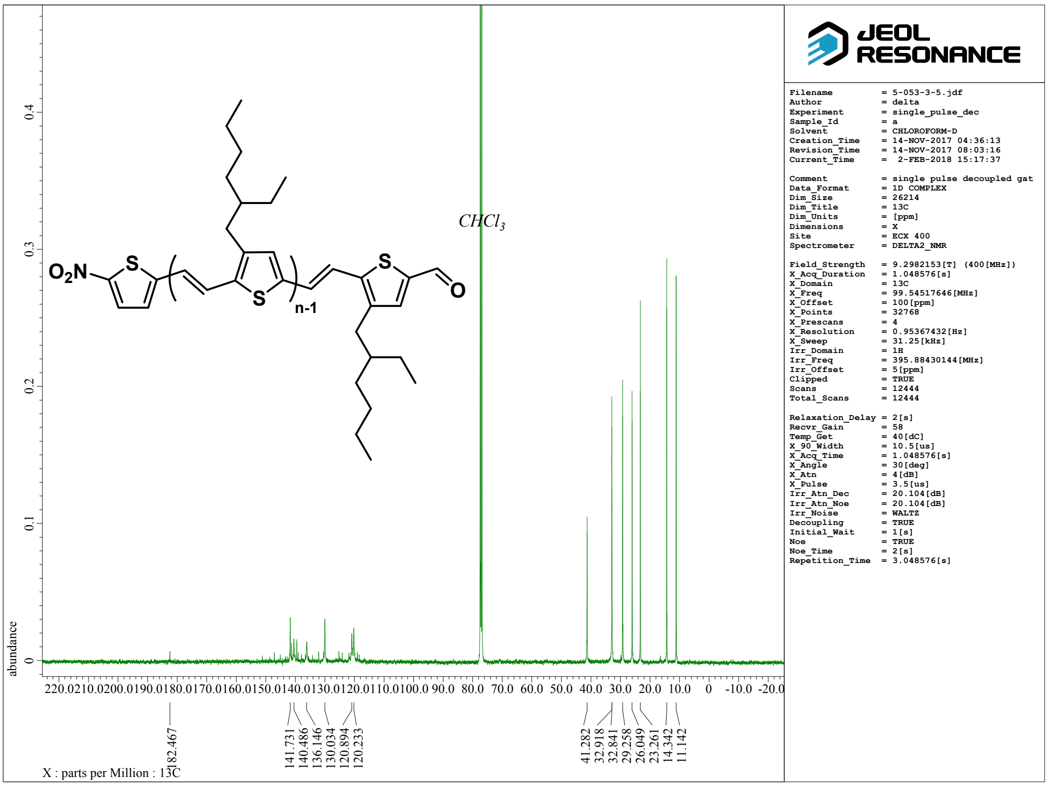
```
Filename          = 5-053-2-8.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 13-NOV-2017 18:00:30
Revision_Time     =  9-JAN-2018 18:35:53
Current_Time      =  9-JAN-2018 18:35:59

Comment           = single_pulse
Data_Format       = 1D COMPLEX
Dim_Size          = 13107
Dim_Title         = 1H
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 2.20725248[s]
X_Domain          = 1H
X_Freq            = 395.88430144[MHz]
X_Offset          = 5[ppm]
X_Points          = 16384
X_Prescans        = 1
X_Resolution      = 0.45305193[Hz]
X_Sweep           = 7.42280285[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Tri_Domain        = 1H
Tri_Freq          = 395.88430144[MHz]
Tri_Offset        = 5[ppm]
Clipped           = FALSE
Scans             = 160
Total_Scans       = 160

Relaxation_Delay = 5[s]
Recvr_Gain        = 36
Temp_Get          = 40[dC]
X_90_Width        = 12.75[us]
X_Acq_Time        = 2.20725248[s]
X_Angle           = 45[deg]
X_Atn             = 1[dB]
X_Pulse           = 6.375[us]
Irr_Mode          = Off
Tri_Mode          = Off
Dante_Presat      = FALSE
Initial_Wait      = 1[s]
Repetition_Time   = 7.20725248[s]
```

(c)



```
Filename          = 5-053-3-5.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_Id         = a
Solvent           = CHLOROFORM-D
Creation_Time     = 14-NOV-2017 04:36:13
Revision_Time     = 14-NOV-2017 08:03:16
Current_Time      =  2-FEB-2018 15:17:37

Comment           = single pulse decoupled gat
Data_Format       = 1D COMPLEX
Dim_Size          = 26214
Dim_Title         = 13C
Dim_Units         = [ppm]
Dimensions        = X
Site              = ECX 400
Spectrometer      = DELTA2_NMR

Field_Strength    = 9.2982153[T] (400[MHz])
X_Acq_Duration    = 1.048576[s]
X_Domain          = 13C
X_Freq            = 99.54517646[MHz]
X_Offset          = 100[ppm]
X_Points          = 32768
X_Prescans        = 4
X_Resolution      = 0.95367432[Hz]
X_Sweep           = 31.25[kHz]
Irr_Domain        = 1H
Irr_Freq          = 395.88430144[MHz]
Irr_Offset        = 5[ppm]
Clipped           = TRUE
Scans             = 12444
Total_Scans       = 12444

Relaxation_Delay  = 2[s]
Recvr_Gain        = 58
Temp_Get          = 40[dC]
X_90_Width        = 10.5[us]
X_Acq_Time        = 1.048576[s]
X_Angle           = 30[deg]
X_Atn             = 4[dB]
X_Pulse           = 3.5[us]
Irr_Atn_Dec       = 20.104[dB]
Irr_Atn_Noe       = 20.104[dB]
Irr_Noise         = WALTZ
Decoupling        = TRUE
Initial_Wait      = 1[s]
Noe               = TRUE
Noe_Time          = 2[s]
Repetition_Time   = 3.048576[s]
```

Figure S7. (a) ^{1}H NMR, (b) magnified ^{1}H NMR and (c) ^{13}C NMR spectra of P3EHTV (Run 6).

SEC UV traces of P3EHTV

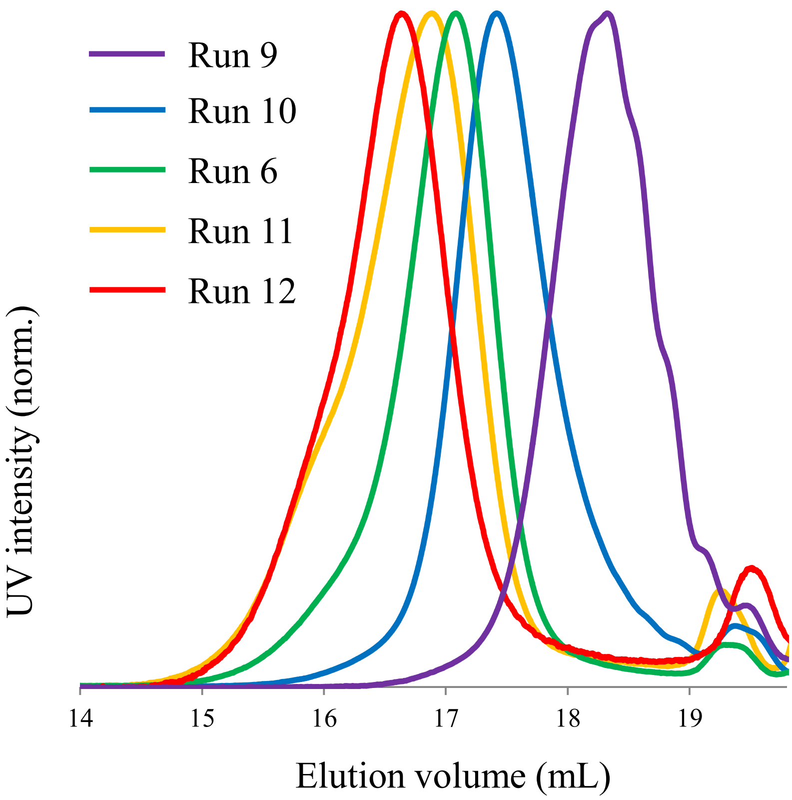


Figure S8. SEC UV traces of unfractionated P3EHTV samples with a different [**1a**]/[**2a**] ratio (Runs 6 and 9-12).

Polymerization rate

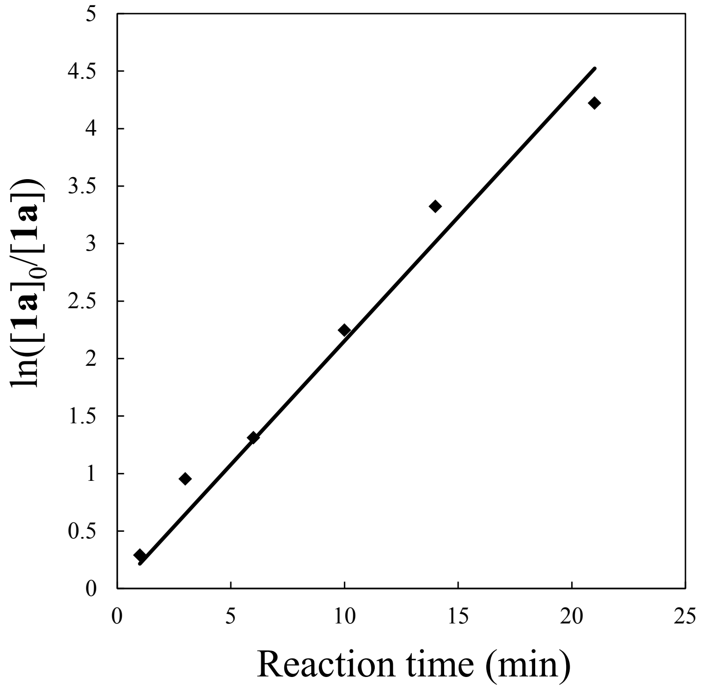


Figure S9. The plots of ln([**1a**]$_0$/[**1a**]) as a function of time for synthesizing P3EHTV.

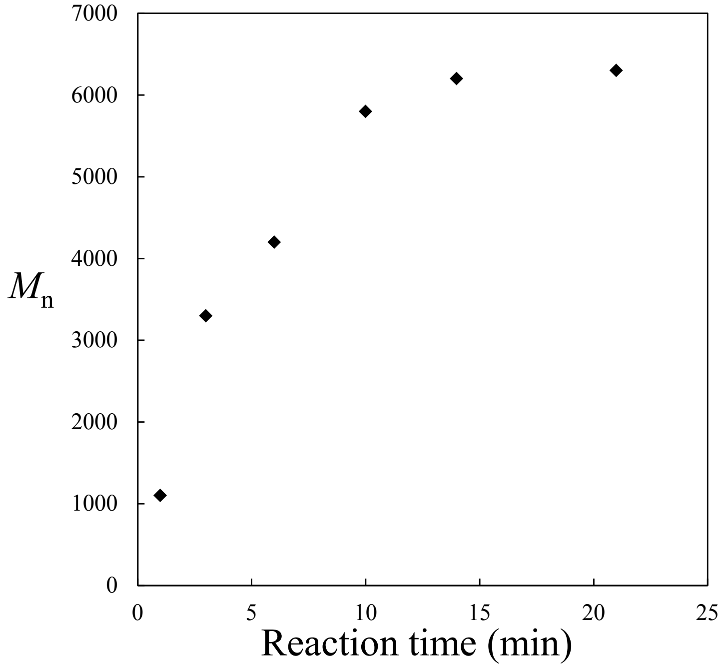


Figure S10. The plots of M_n as a function of time for synthesizing P3EHTV.

GIWAXS

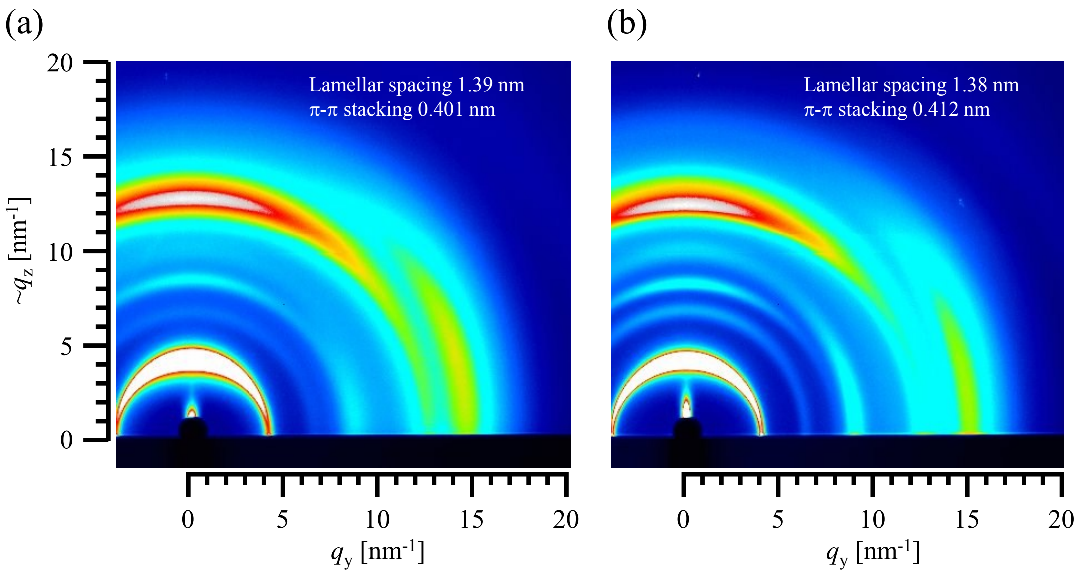


Figure S11. 2D-GIWAXS images of P3EHTV. Films were spin-cast on a Si wafer (a) without annealing and (b) with annealing at 150 ºC for 1 h under vacuum.

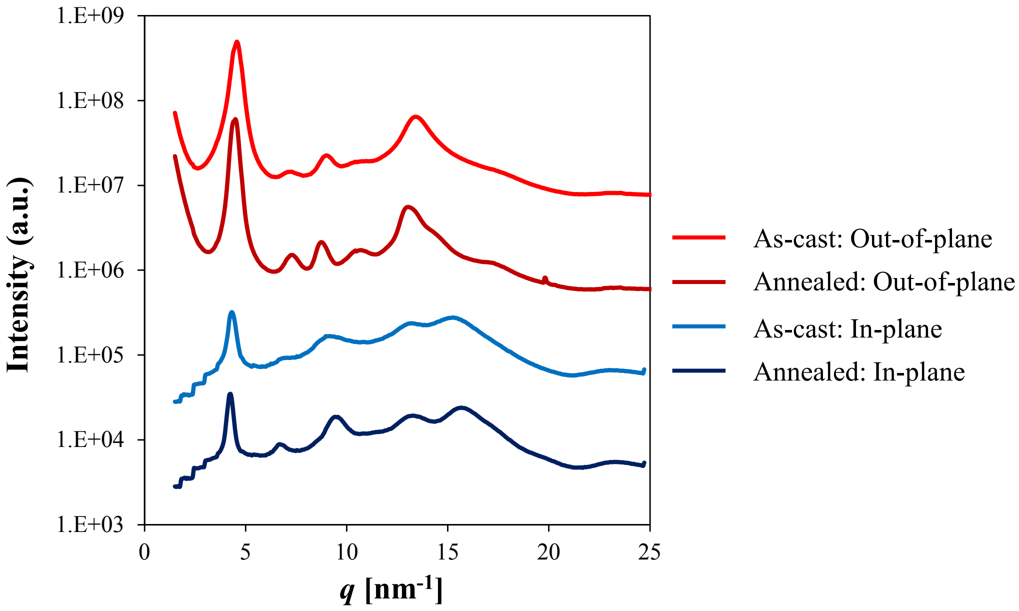


Figure S12. 1D-GIWAXS profiles of P3EHTV. Films were spin-cast on a Si wafer with or without annealing at 150 ºC for 1 h under vacuum.

TGA thermograms

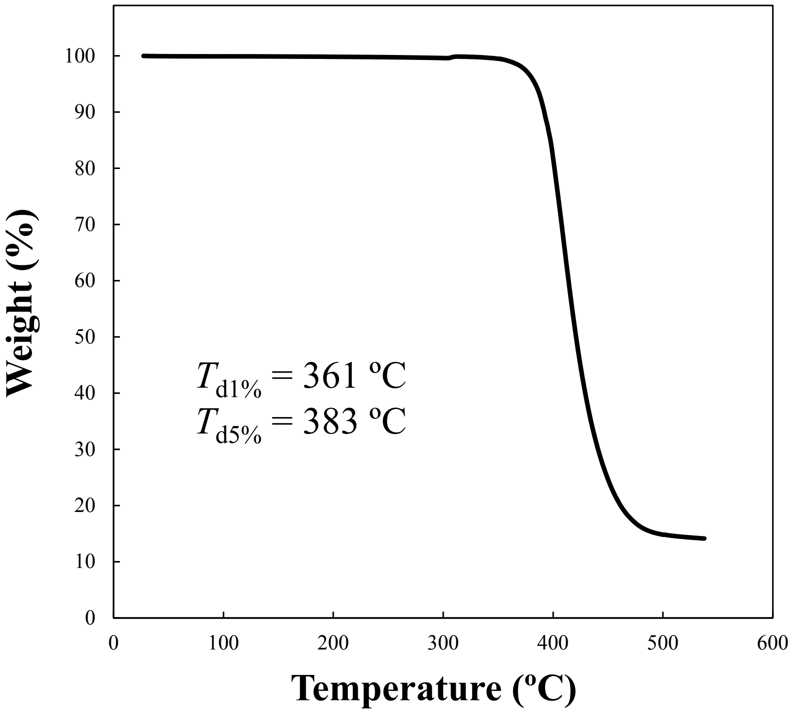


Figure S13. TGA curve of P3EHTV at a heating scan rate of 10 °C/min in N_2.

DSC thermograms

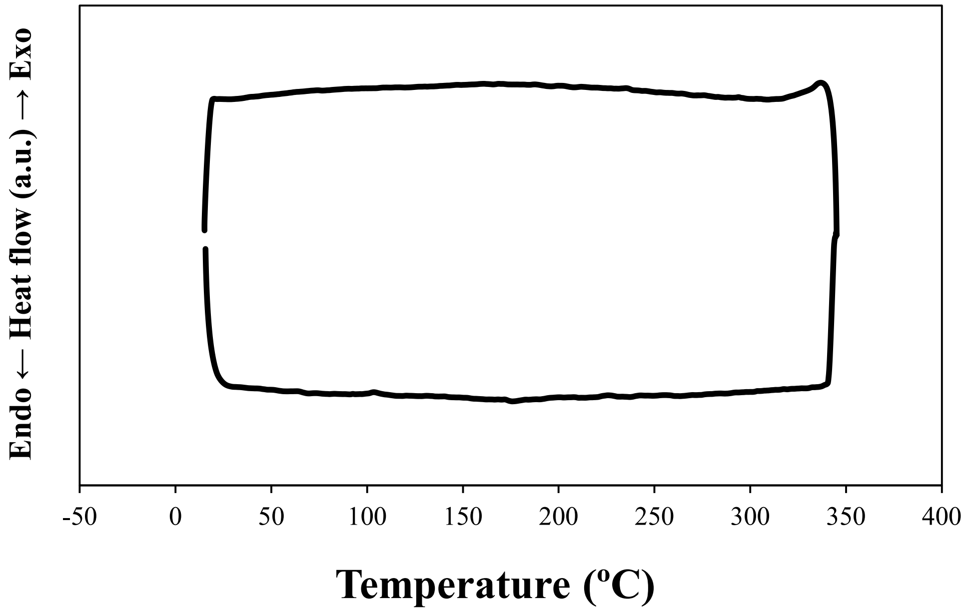


Figure S14. DSC curve of the 2^{nd} cycle heating and 2^{nd} cycle cooling scans of P3EHTV (10 °C/min in N_2).

UV-vis absorption

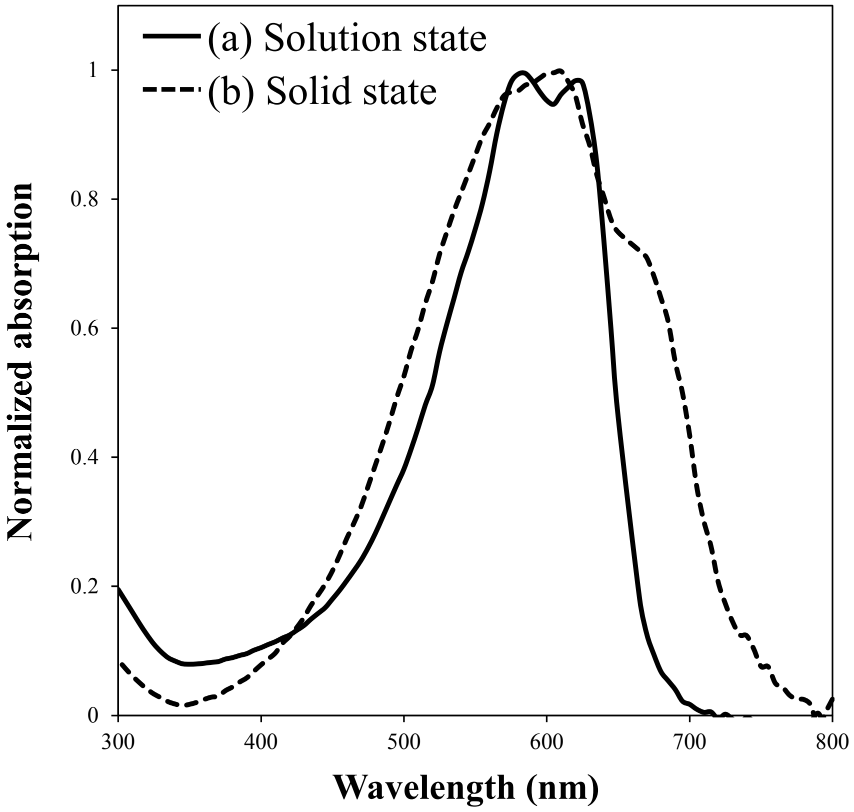


Figure S15. UV-vis absorption spectra of P3EHTV (a) in chloroform and (b) drop-cast from chloroform and annealed at 150 °C at 1 h under vacuum.

Table S1. Optical properties of P3EHTV

	λ_{max} (nm)	λ_{onset} (nm)	E_{g} (eV)
Solution state	578	670	1.85
Film state	603	742	1.67

Optical properties were determined by UV-vis spectroscopy.

Reference

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