

## Electronic Supplementary Information

### Highly Efficient and Facile Alkylation of 4*H*-Cyclopenta [2,1-*b*:3,4-*b'*] dithiophene in Water

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#### Table of contents

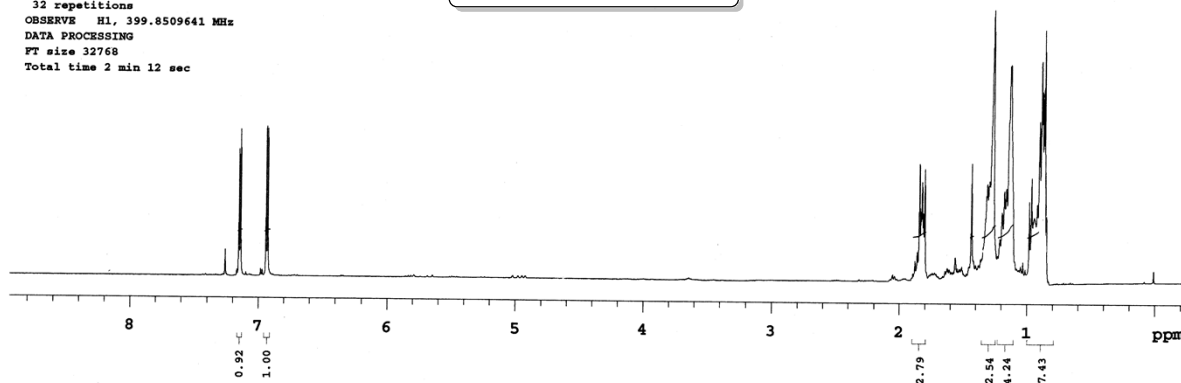
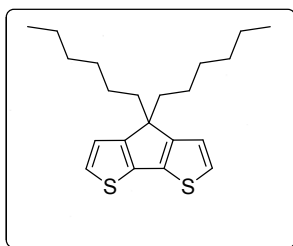
1. 4,4'-Dialkyl-4 <i>H</i> -cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i> ]dithiophene NMR( <sup>1</sup> H, <sup>13</sup> C) and HRMS spectra	S2-S13
2. 2,6-Dibromo-4,4'-Dialkyl-4 <i>H</i> -cyclopenta[2,1- <i>b</i> :3,4- <i>b'</i> ]dithiophene NMR( <sup>1</sup> H, <sup>13</sup> C) and HRMS spectra	S14-S25
3. 2,6-Dibromo spiro[4,5] ([2,1- <i>b</i> ; 3,4- <i>b'</i> ]dithieno)decane NMR ( <sup>1</sup> H, <sup>13</sup> C) and Crystal data	S25-S26

TBR-CPDT-C6

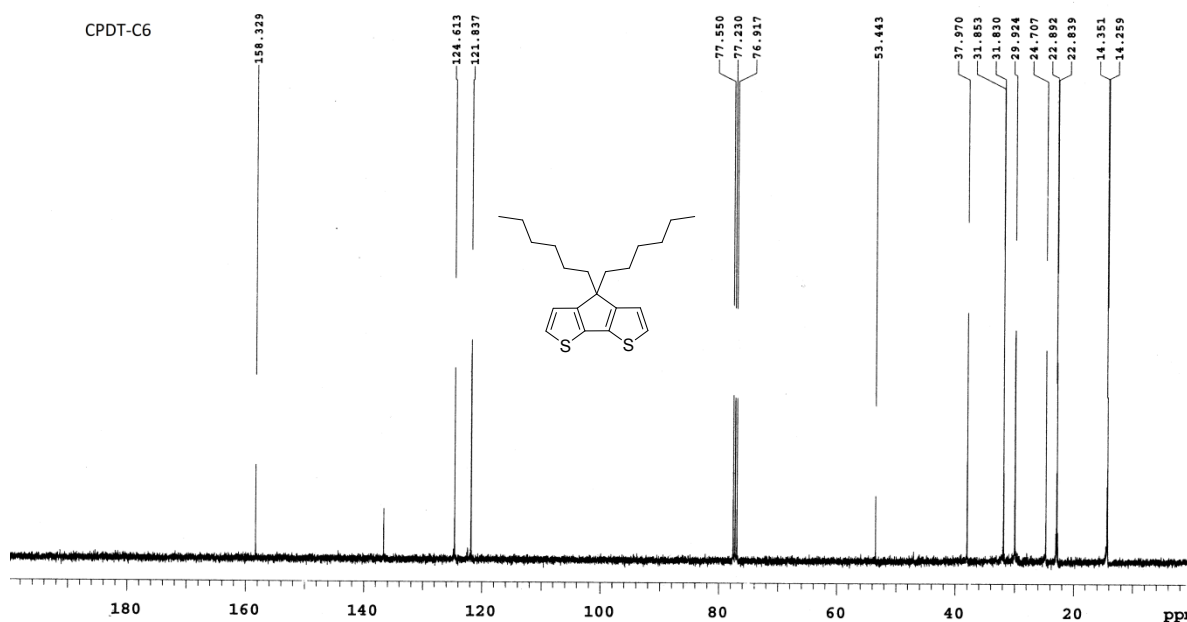
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Archive directory:  
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Sample directory:  
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FidFile: TBR-CPDT-C6  
Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: Dec 20 2013

Temp. 25.0 C / 298.1 K  
Operator: chem

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 2.561 sec  
Width 6398.0 Hz  
32 repetitions  
OBSERVE H1, 399.8509641 MHz  
DATA PROCESSING  
FT size 32768  
Total time 2 min 12 sec



**Figure S1:**  $^1\text{H}$ -NMR spectrum of 4,4'-Dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1a).



**Figure S2:**  $^{13}\text{C}$ -NMR spectrum of 4,4'-Dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1a).

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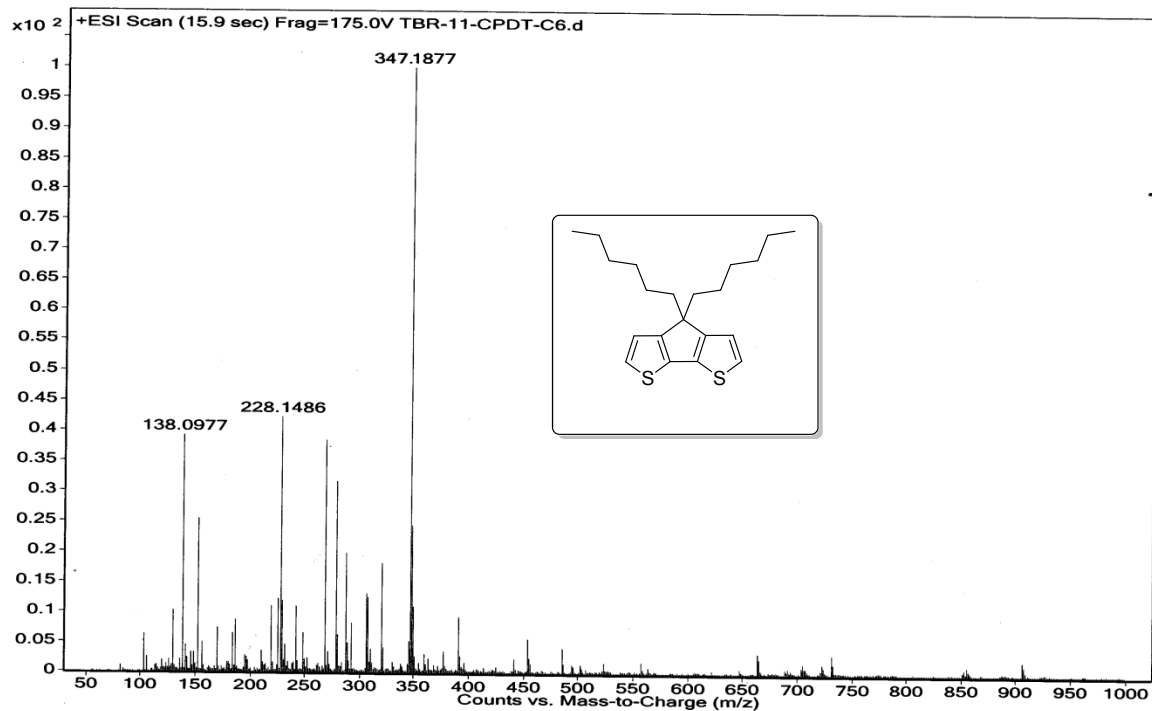


Figure S3: ESI-MS spectrum of 4,4'-Dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1a).

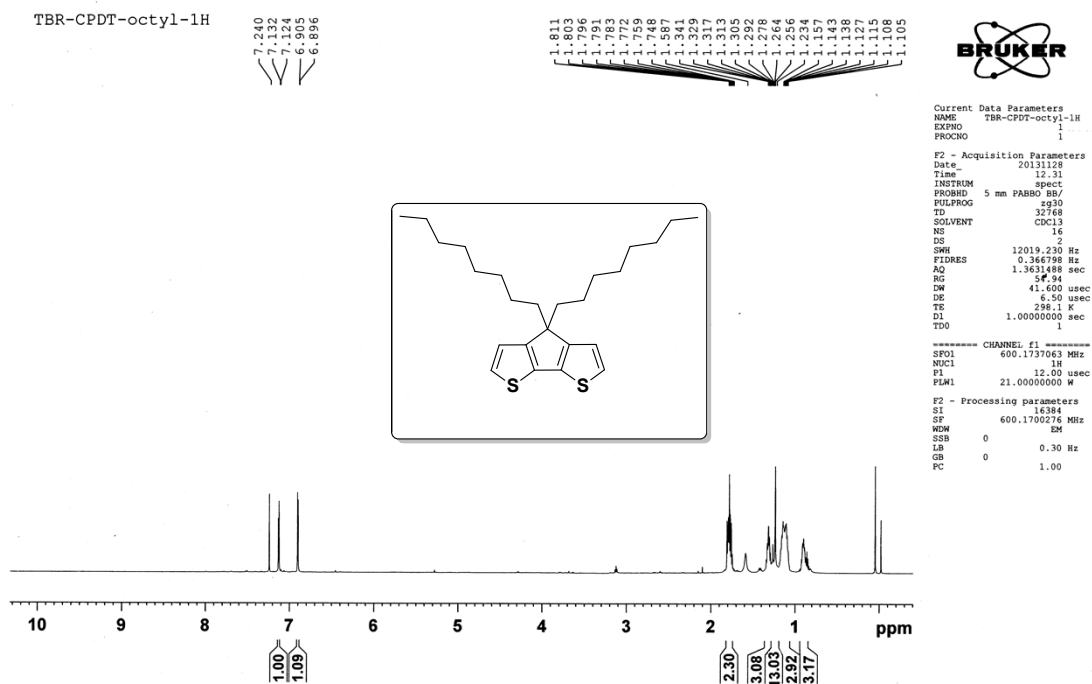
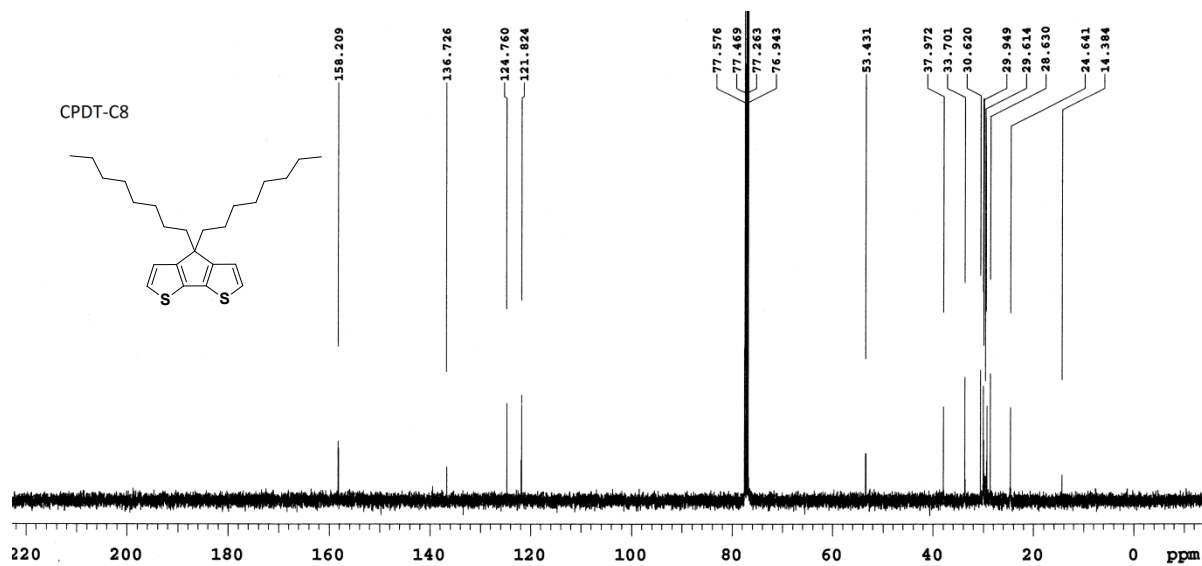
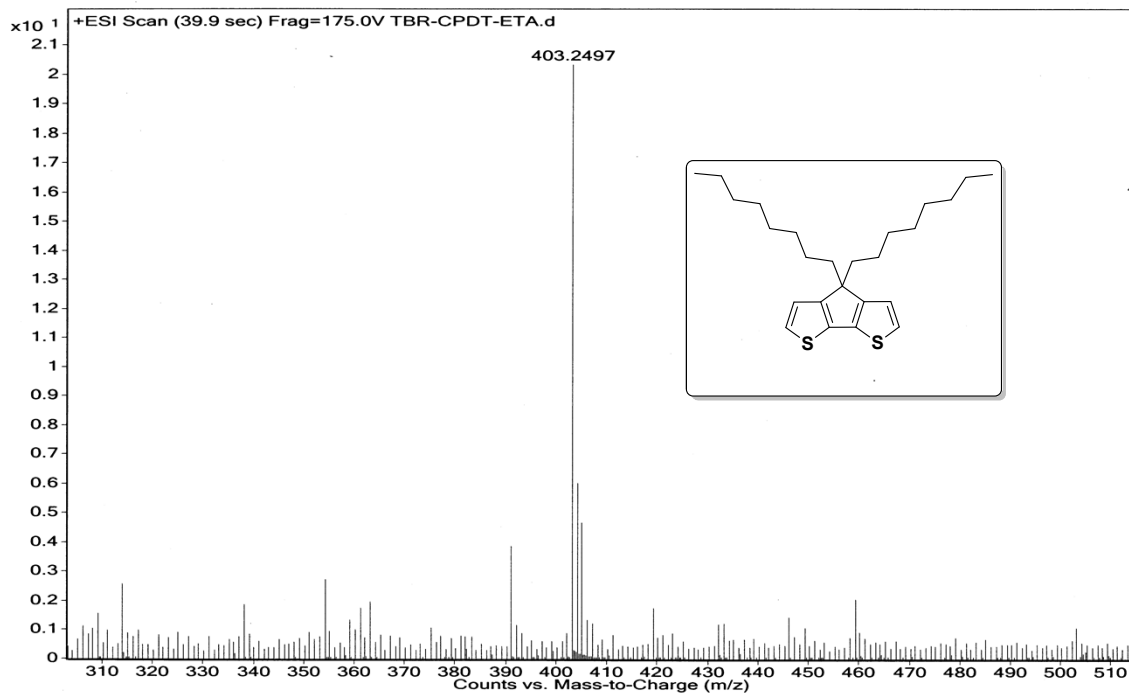


Figure S4: <sup>1</sup>H-NMR spectrum of 4,4'-Dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1b).



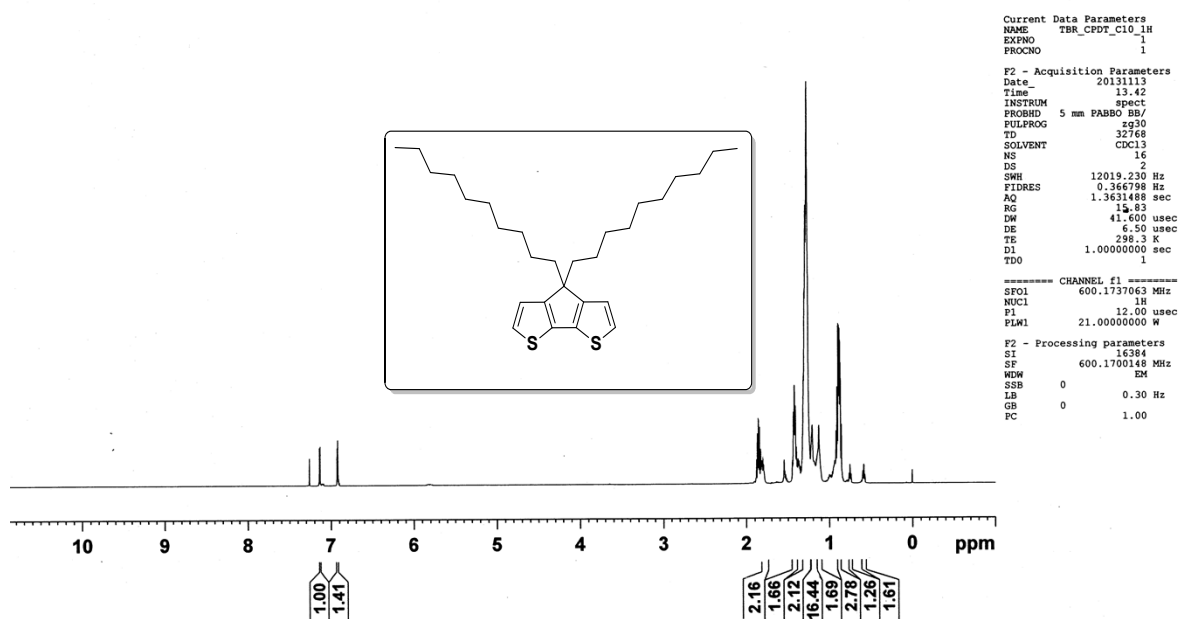
**Figure S5:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Dioctyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1b).

Sample Name	TBR CPDT-C <sub>8</sub>	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
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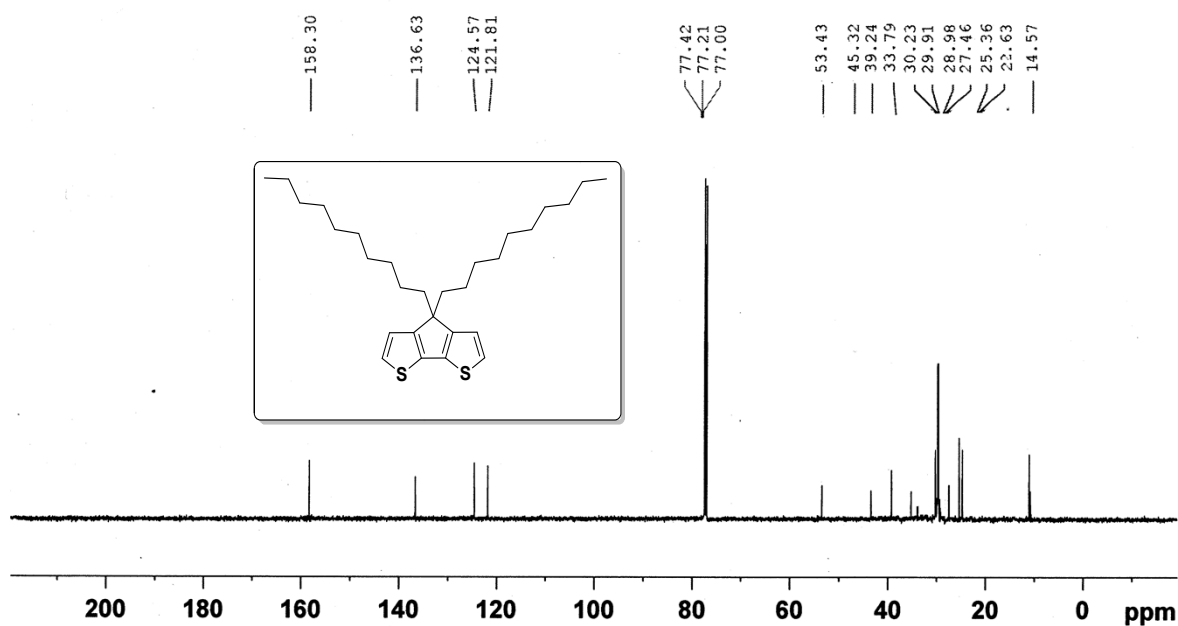
**Figure S6:** ESI-MS spectrum of 4,4'-Dioctyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1b).

TBR\_CPDT\_C10\_H



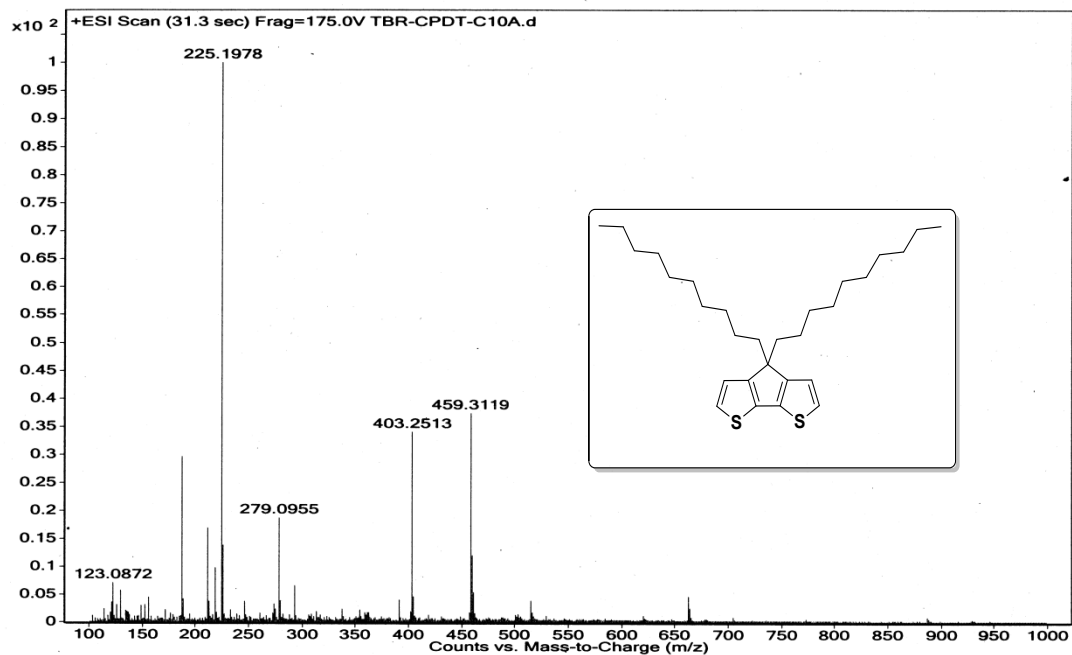
**Figure S7:**  $^1\text{H}$ -NMR spectrum of 4,4'-Bisdecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1c).

TBR\_CPDT\_C10\_13C

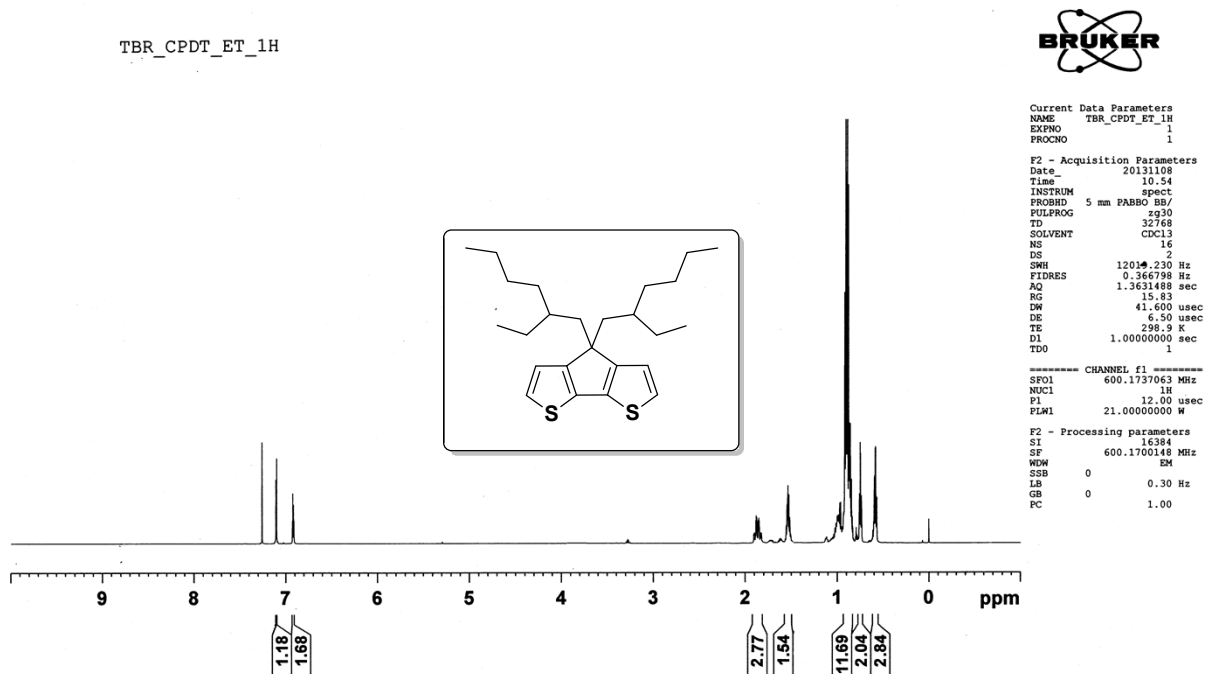


**Figure S8:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bisdecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1c).

Sample Name	TBR-CPDT-C10A	Position	-1	Instrument Name	Instrument 1	User Name	
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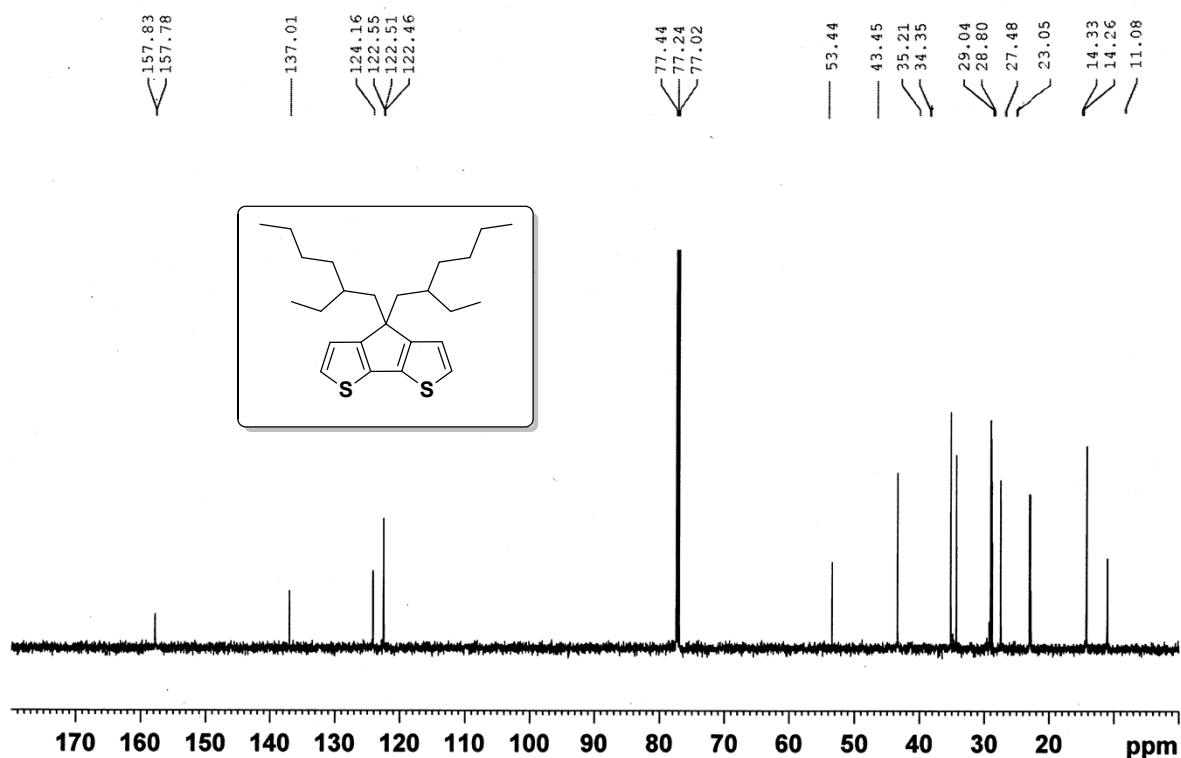


**Figure S9:** ESI-MS spectrum of 4,4'-Bisdecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1c).



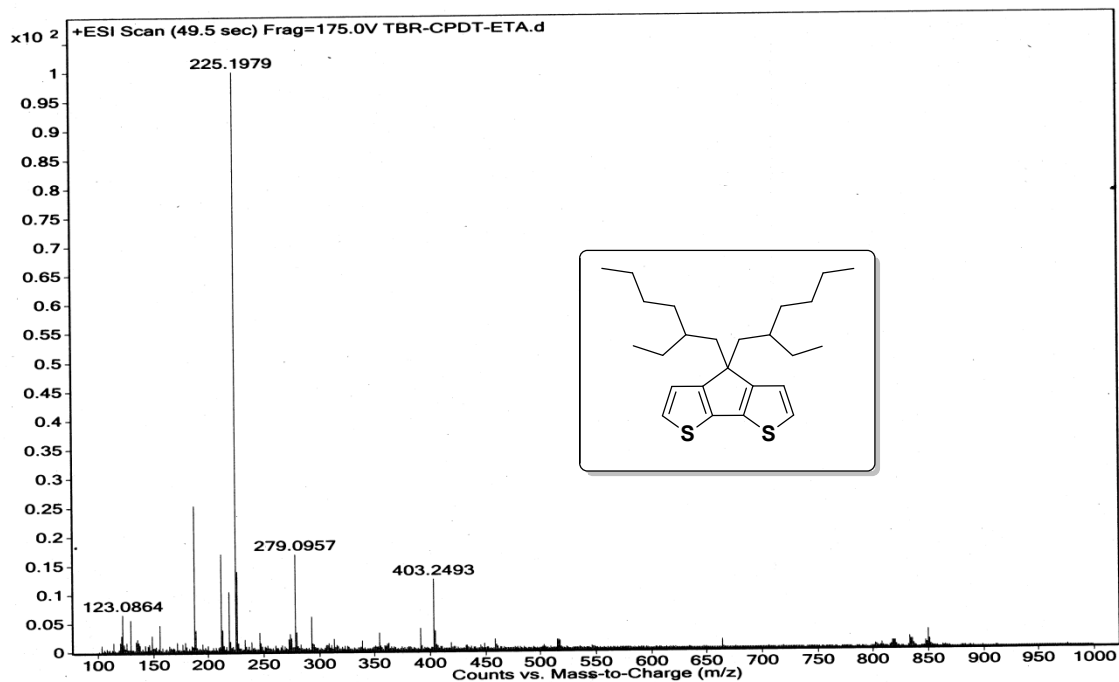
**Figure S10:** <sup>1</sup>H-NMR spectrum of 4,4'-Bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1d).

TBR\_CPD\_T ET\_13C

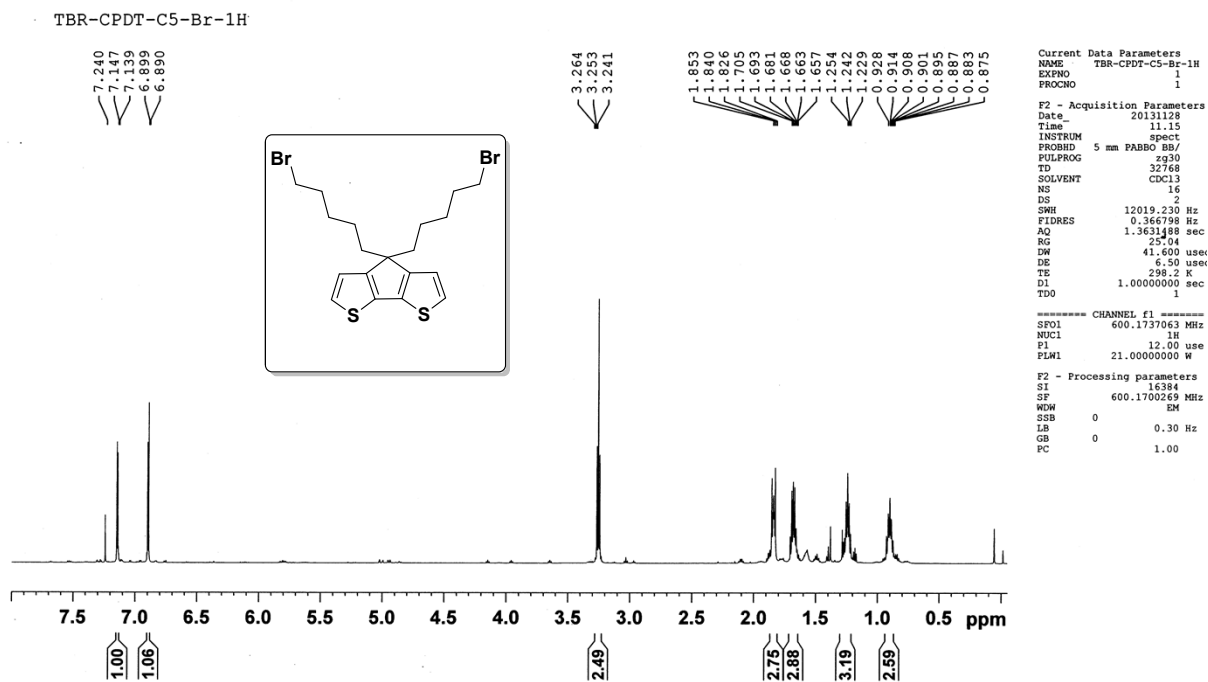


**Figure S11:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1d).

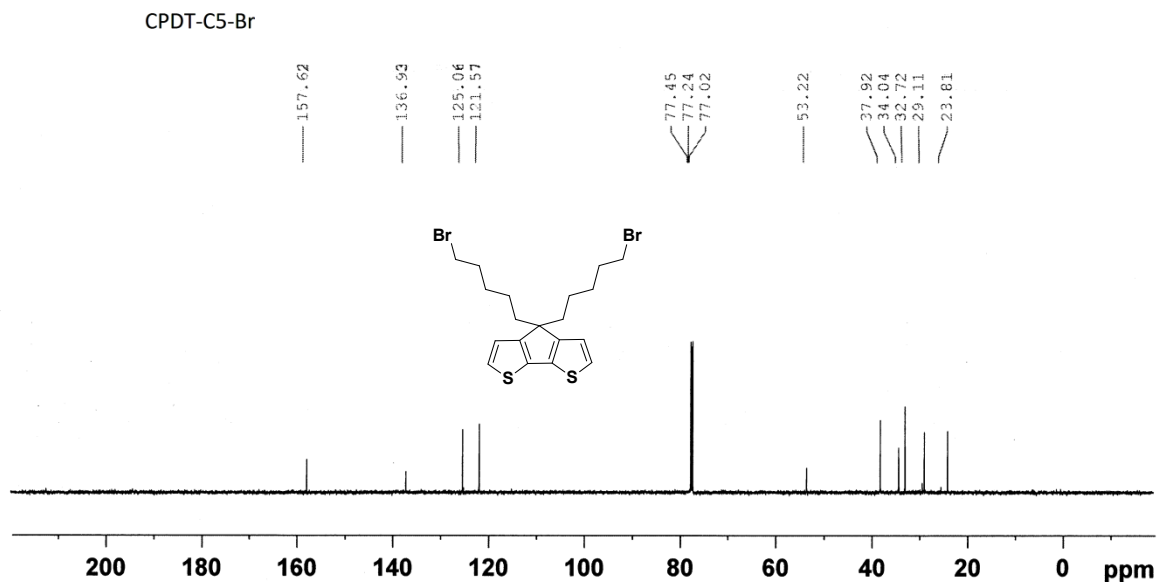
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**Figure S12:** ESI-MS spectrum of 4,4'-Bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1d).



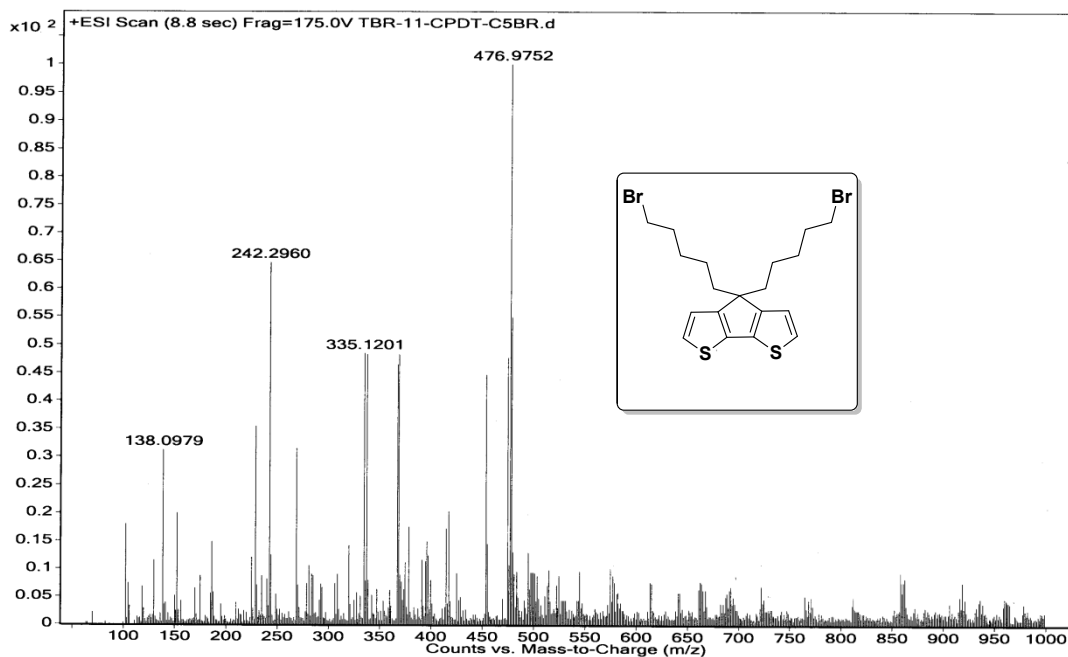
**Figure S13:**  $^1\text{H}$ -NMR spectrum of 4,4'-Bis-(5-bromopentyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1e).



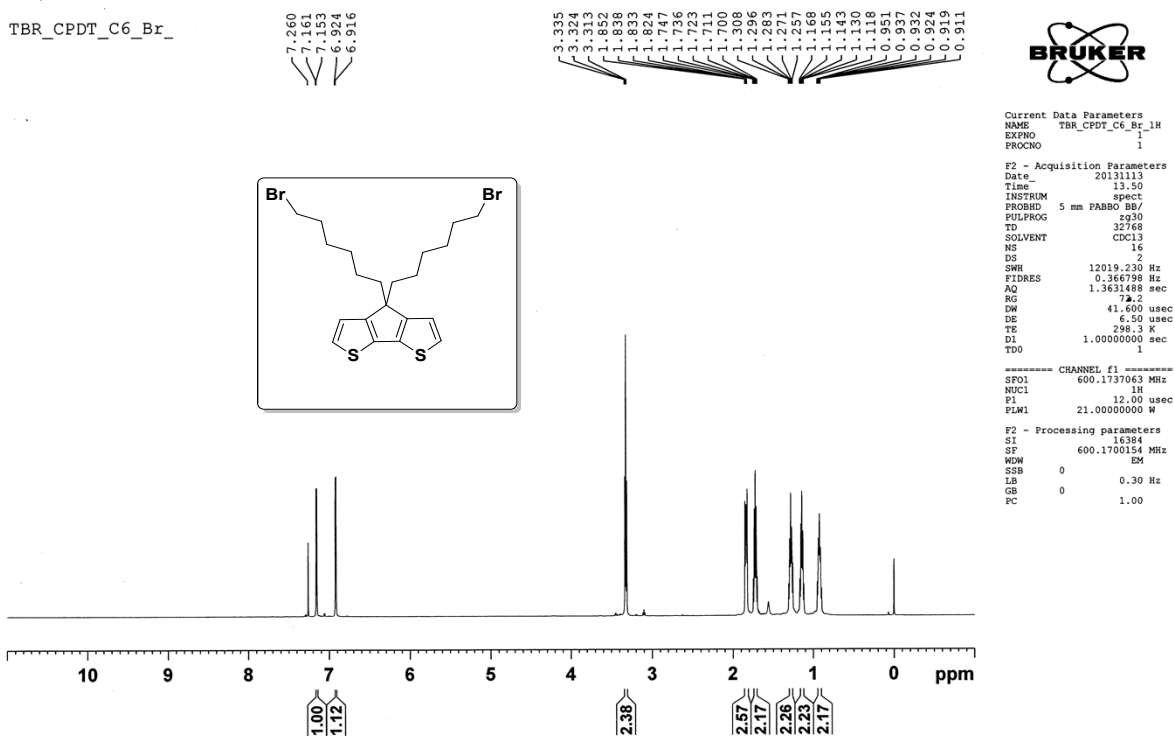
**Figure S14:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis-(5-bromopentyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1e).



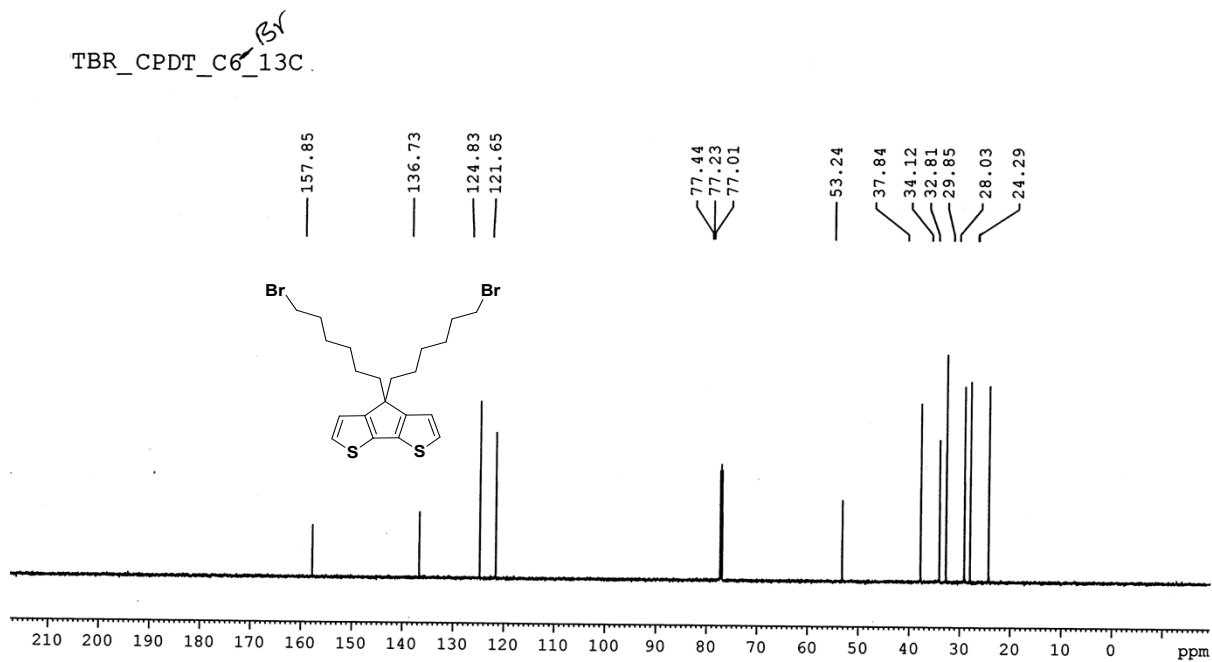
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Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TBR-11-CPDT-C5BR.d	ACQ Method		Comment		Acquired Time	2/14/2014 11:39:37 AM



**Figure S15:** ESI-MS spectrum of 4,4'-Bis-(5-bromopentyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1e).

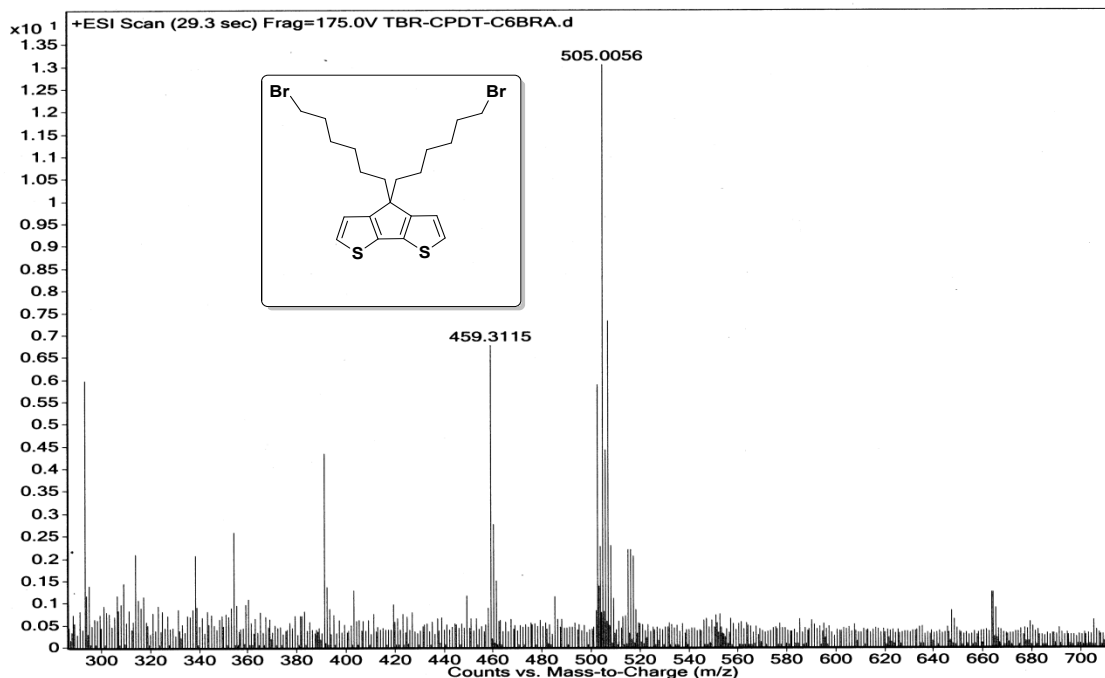


**Figure S16:** <sup>1</sup>H NMR spectrum of 4,4'-Bis-(6-bromohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1f).



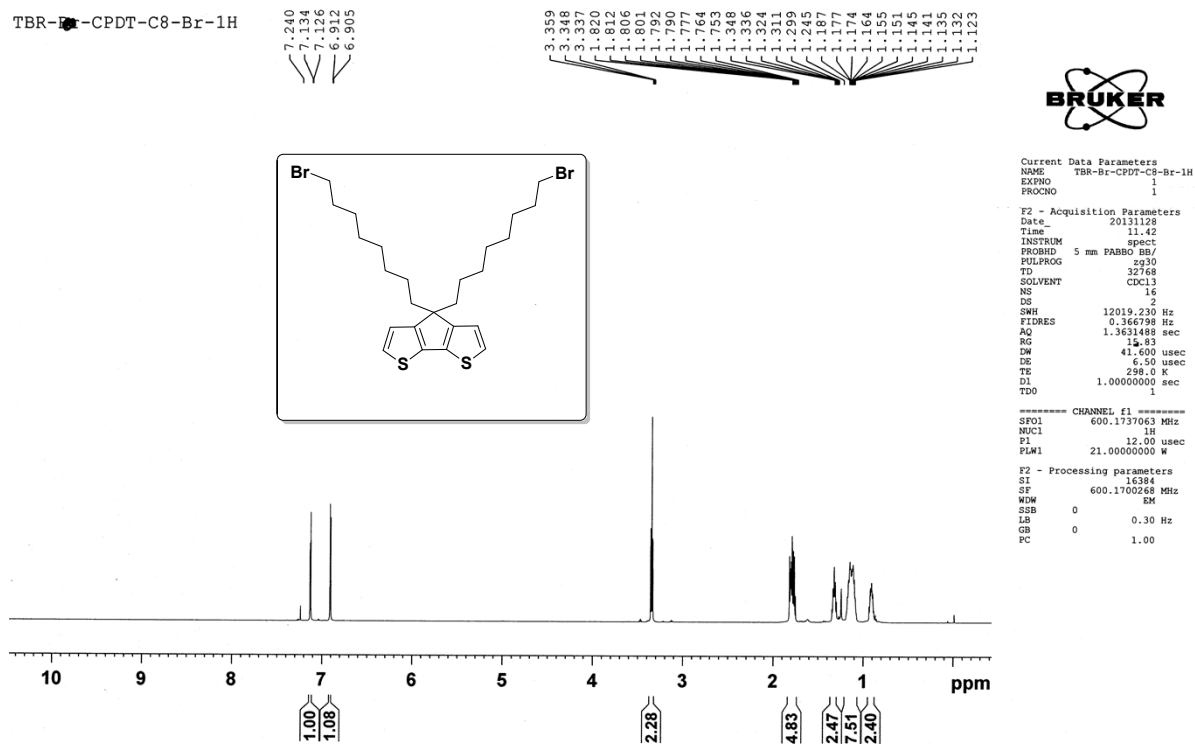
**Figure S17:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis-(6-bromohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1f).

Sample Name	TBR-CPDT-C6BRA	Position	-1	Instrument Name	Instrument 1	User Name	
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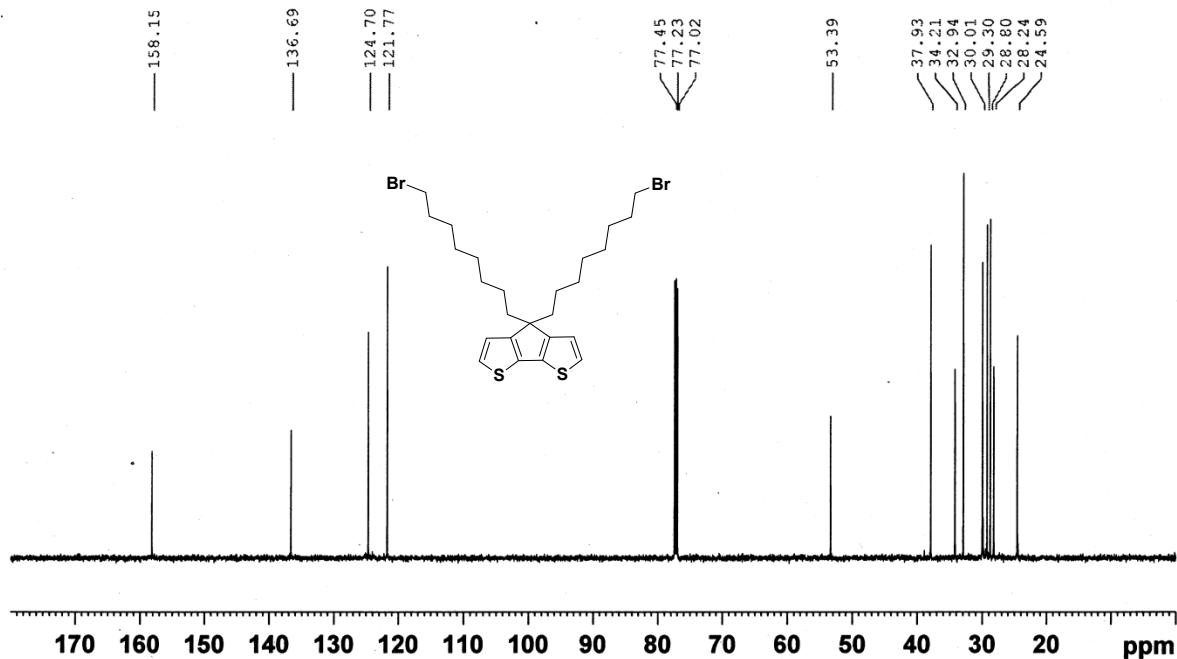
**Figure S18:** ESI-MS spectrum of 4,4'-Bis-(6-bromohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1f).

TBR-CPDT-C8-Br-1H



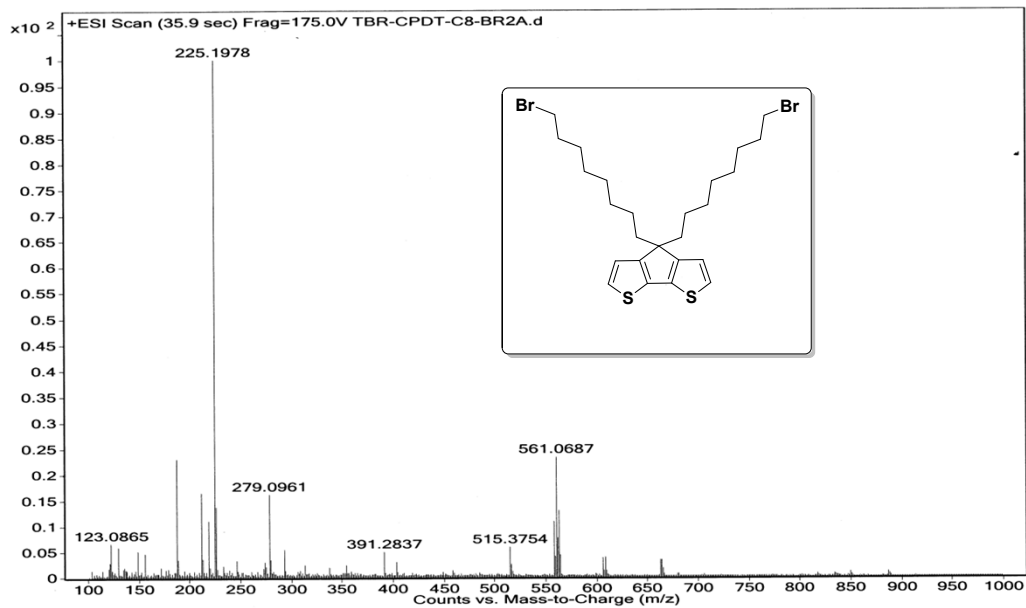
**Figure S19:**  $^1\text{H}$  NMR spectrum of 4,4'-Bis-(8-bromooctyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1g).

CPDT\_C8\_Br\_13C



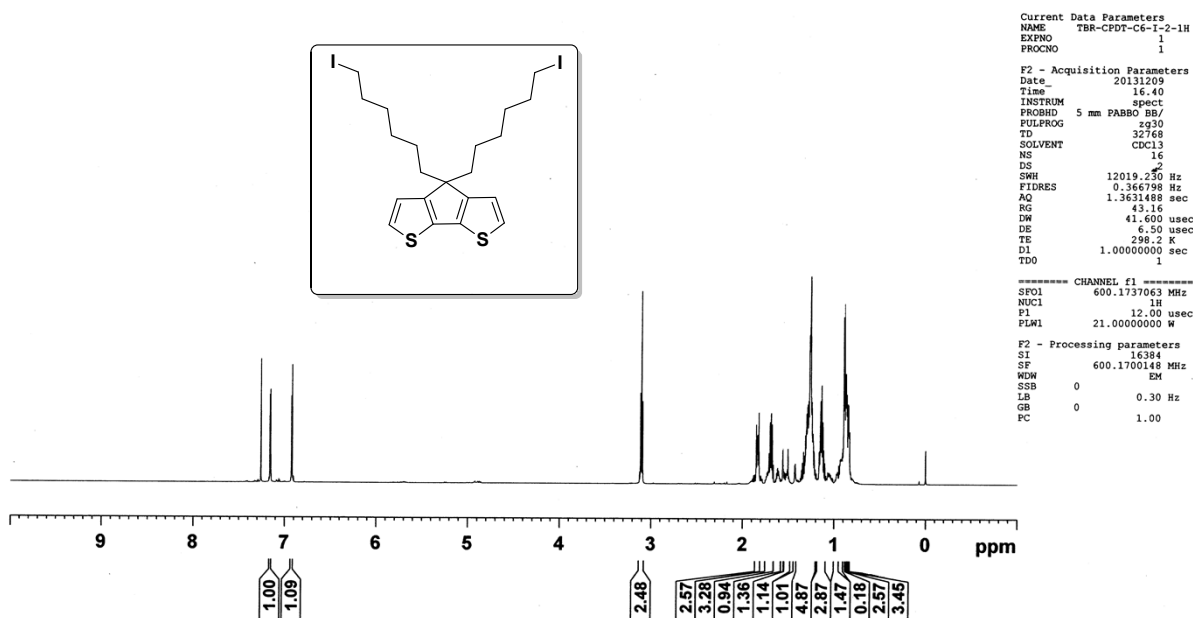
**Figure S20:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis-(8-bromooctyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1g).

Sample Name	TBR-CPDT-C8-BR2A	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TBR-CPDT-C8-BR2A.d	ACQ Method		Comment		Acquired Time	11/14/2013 11:39:24 AM



**Figure S21:** ESI-MS Spectrum of 4,4'-Bis-(8-bromooctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1g).

TBR-CPDT-C6-I-2-1H



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PROCNO   1

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PULPROG  zg30
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DS       2
SWH      12019.230 Hz
FIDRES   0.366798 Hz
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RG       43.16
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DE       6.50 usec
TE       298.2 K
D1       1.00000000 sec
TDO      1

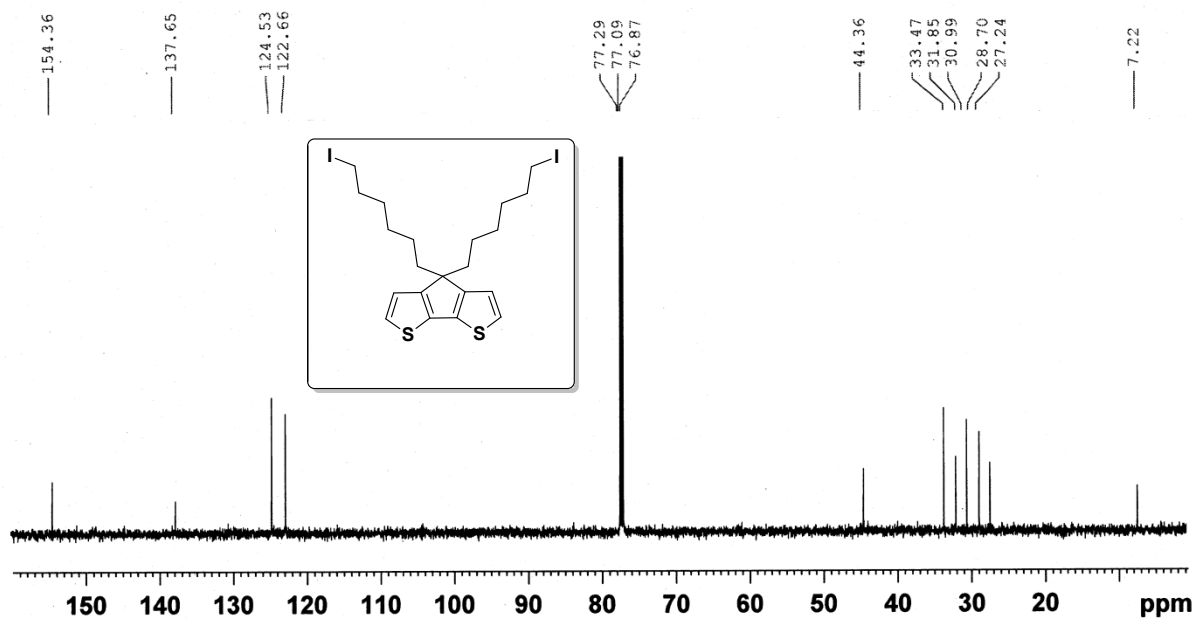
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NUC1     1H
F1       12.00 usec
PLW1     21.00000000 W

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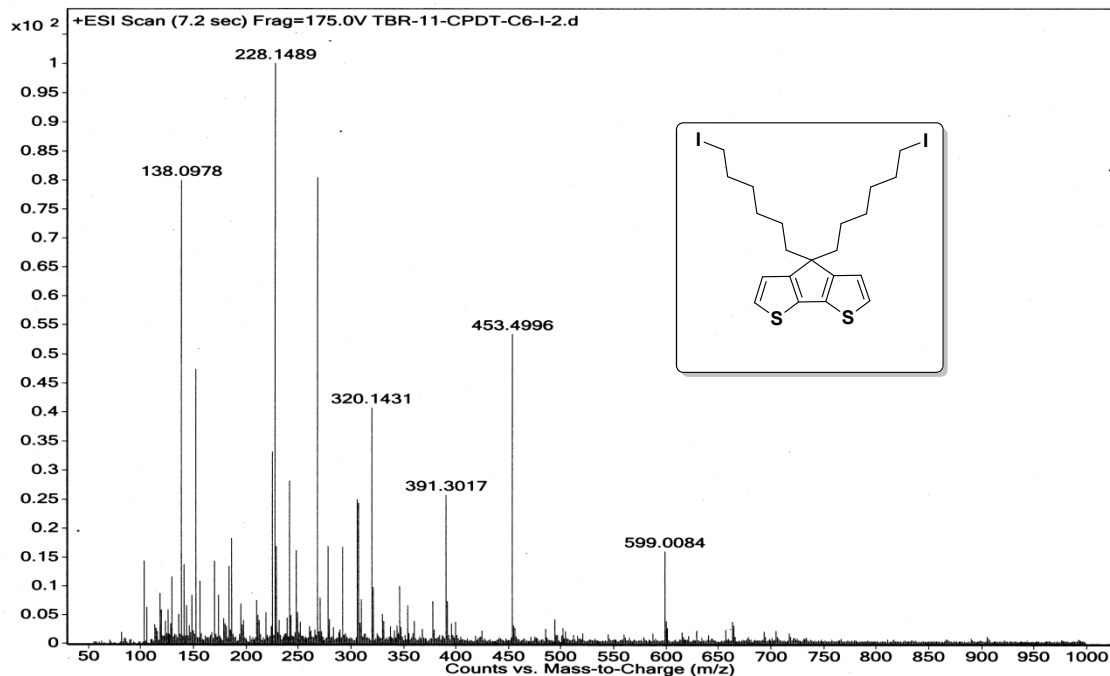
**Figure S22:** <sup>1</sup>H NMR spectrum of 4,4'-Bis-(6-iodohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1h).

TBR-CPDT-C6-I-2\_13C

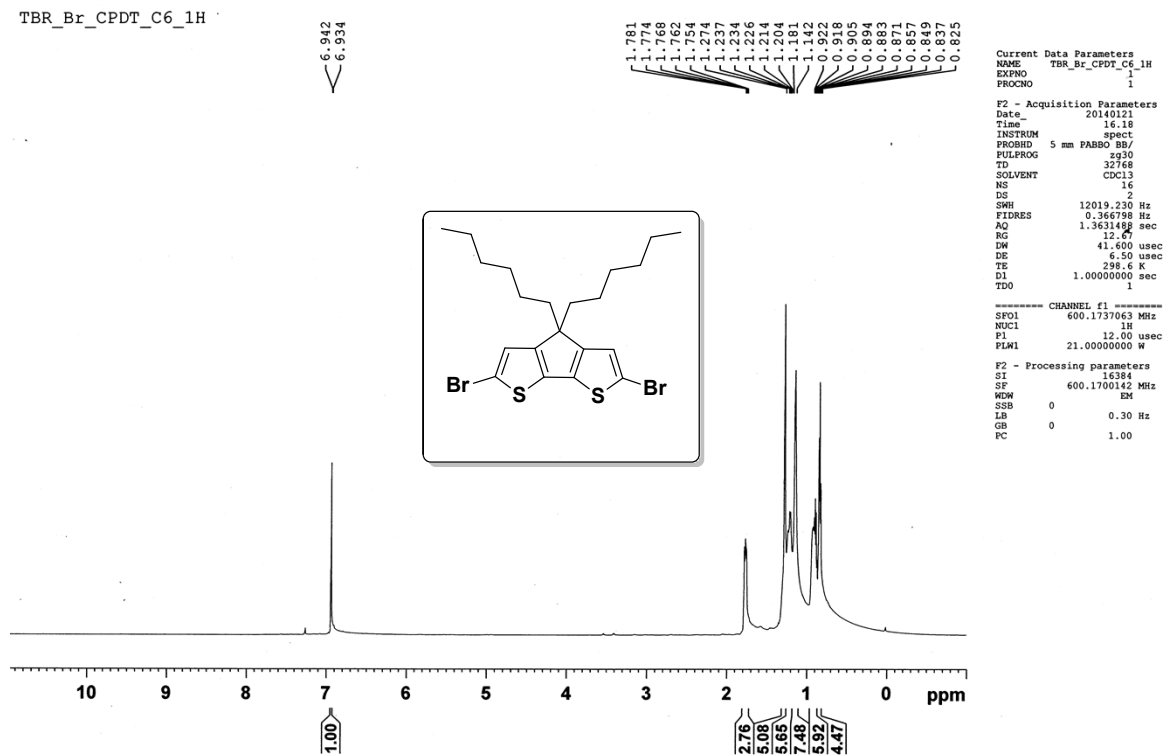


**Figure S23:**  $^{13}\text{C}$  NMR spectrum of 4,4'-Bis-(6-iodohexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1h).

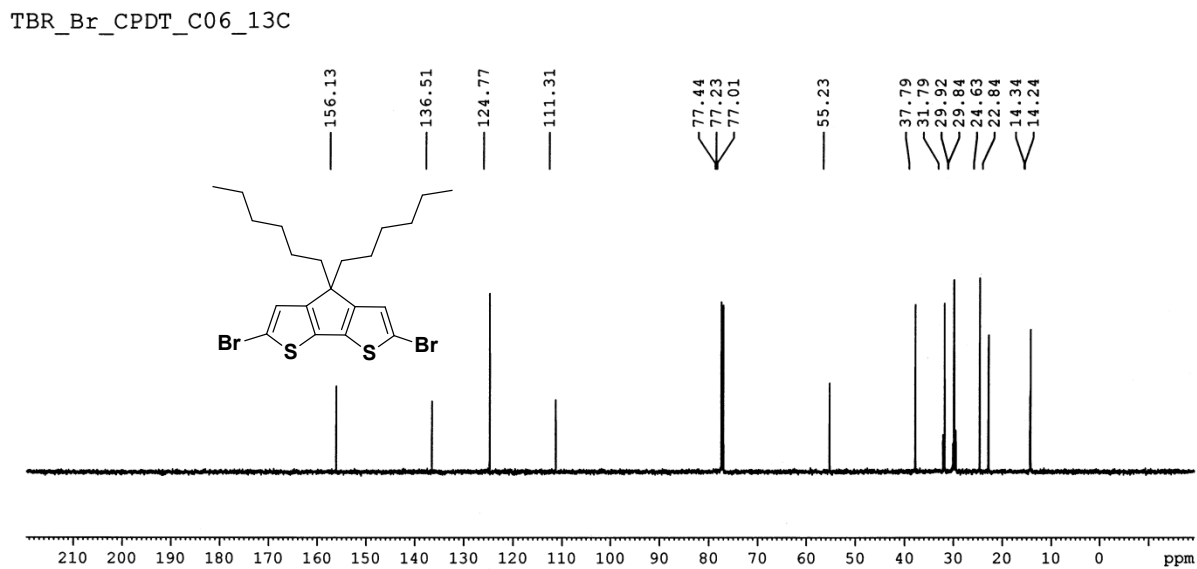
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**Figure S24:** ESI-MS spectrum of spectrum of 4,4'-Bis-(6-iodohexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1h).

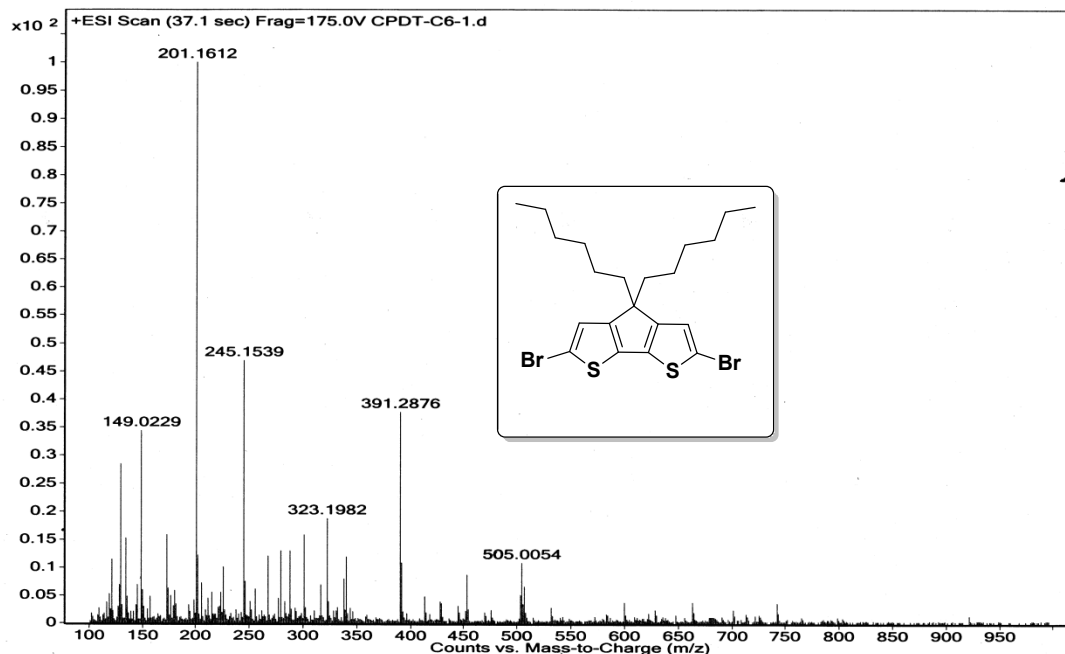


**Figure S25:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1k).



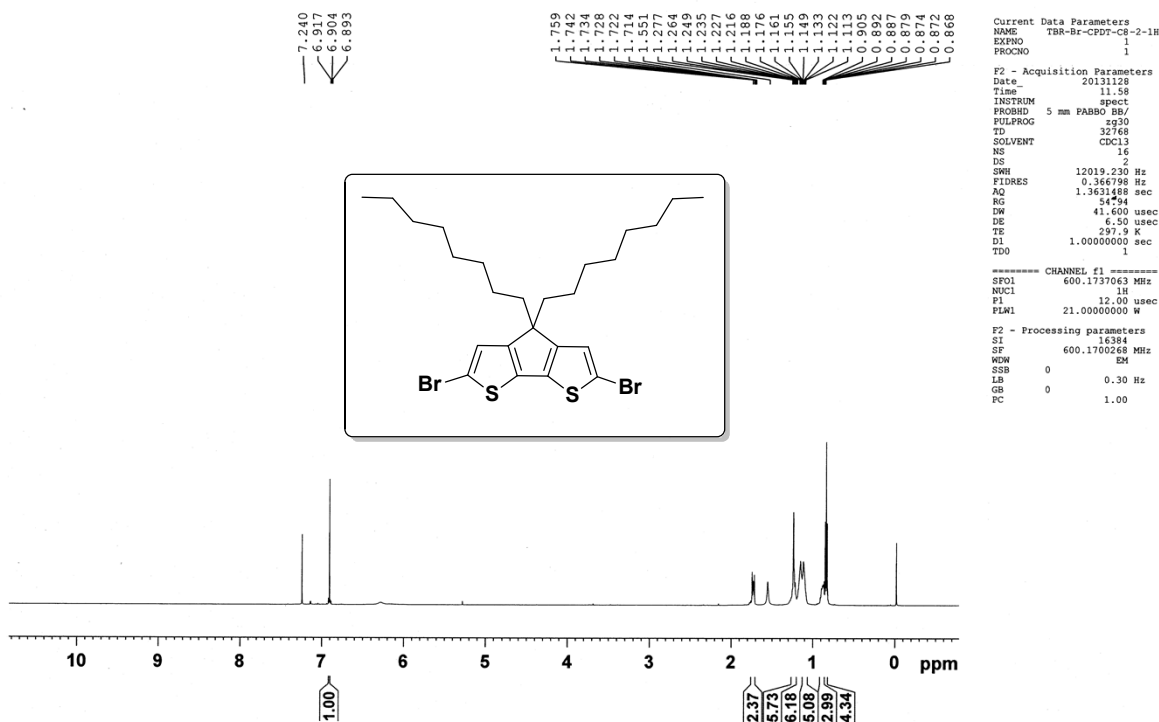
**Figure S26:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (entry 1k).

Sample Name	CPDT-C6-1	Position	-1	Instrument Name	Instrument 1	User Name	
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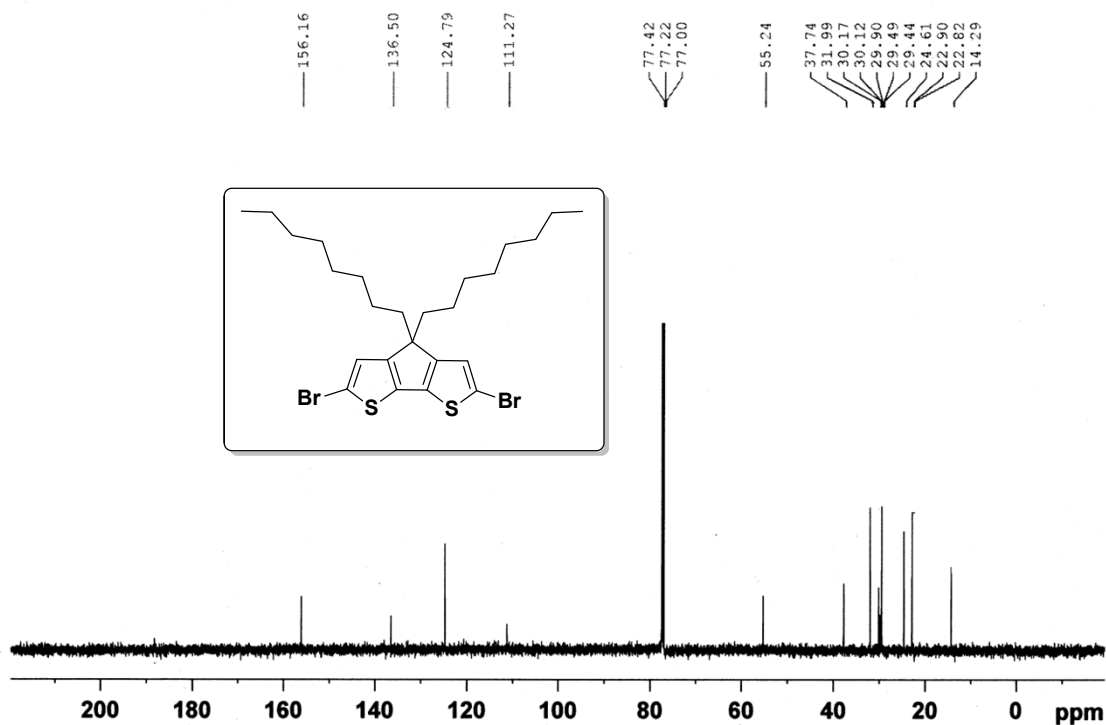
**Figure S27:** ESI-MS spectrum of 2,6-Dibromo-4,4'-diethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1k).

TBR- Br-CPDT-C8-1H



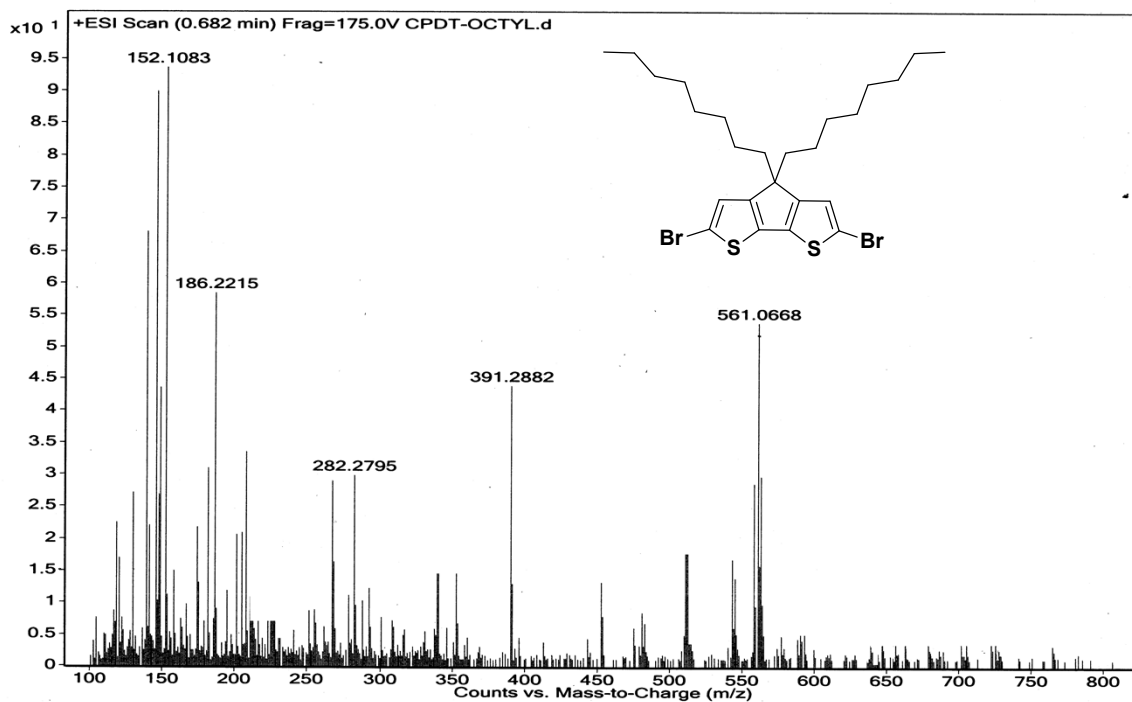
**Figure S28:** <sup>1</sup>H NMR spectrum of 2,6-Dibromo-4,4'-dioctyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1l).

TBR/CPDT\_OCTYL\_13C



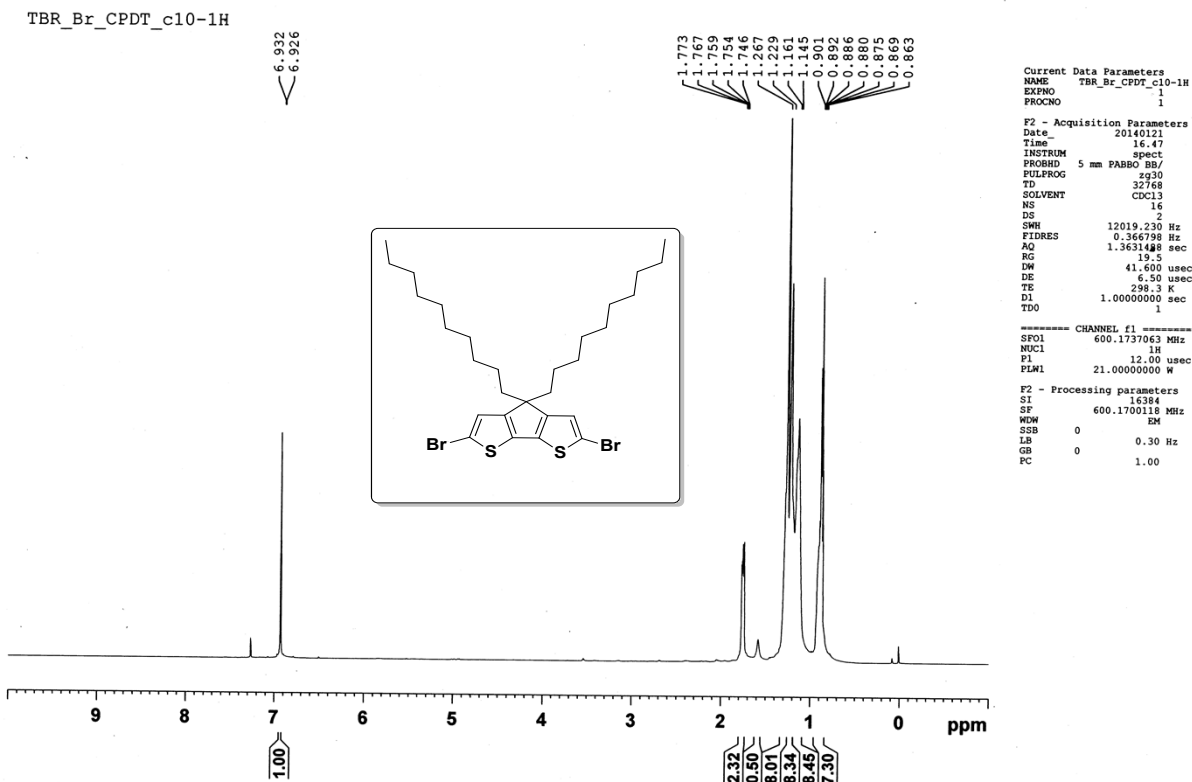
**Figure S29:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-dioctyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 11).

Sample Name	Br-CPDT	Position	-1	Instrument Name	Instrument 1	User Name	
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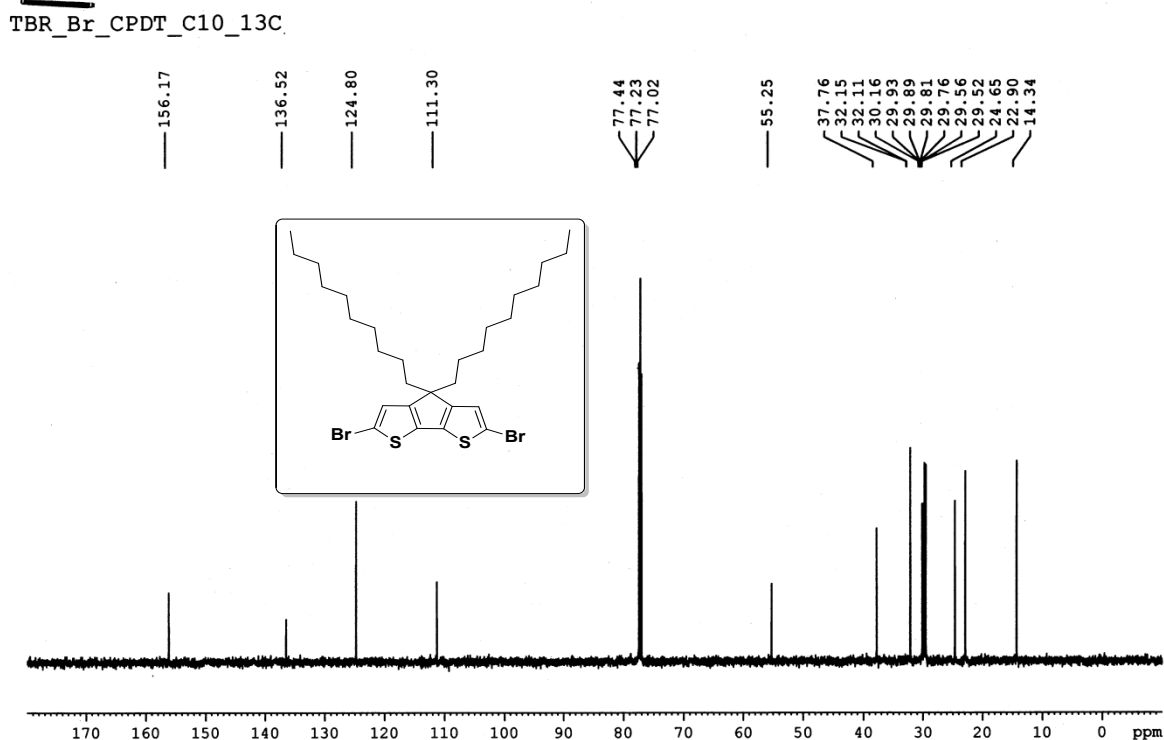


**Figure S30:** ESI-MS spectrum of 2,6-Dibromo-4,4'-dioctyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 11).



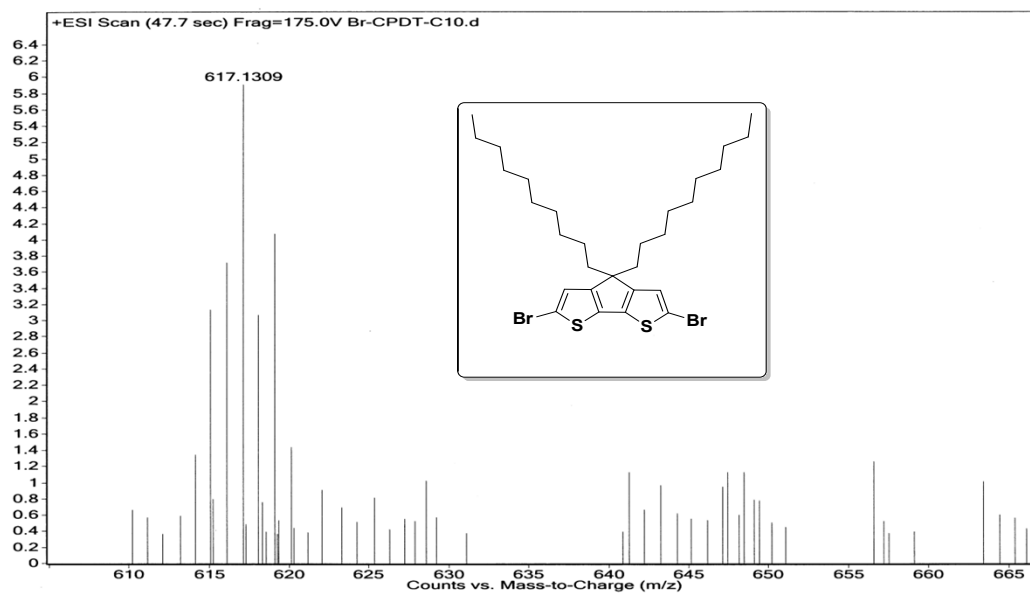


**Figure S31:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-didecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1m).

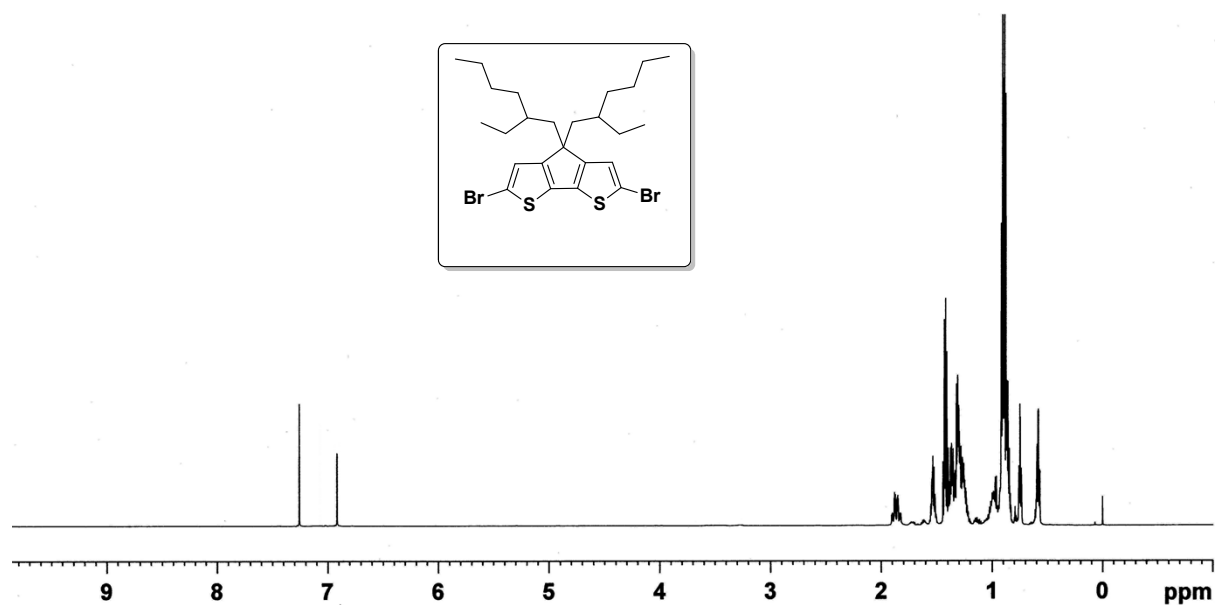


**Figure S32:**  $^{13}\text{C}$  NMR 2,6-Dibromo-4,4'-bisdecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1m).

Sample Name	Br-CPDT-C10	Position	-1	Instrument Name	Instrument 1	User Name	
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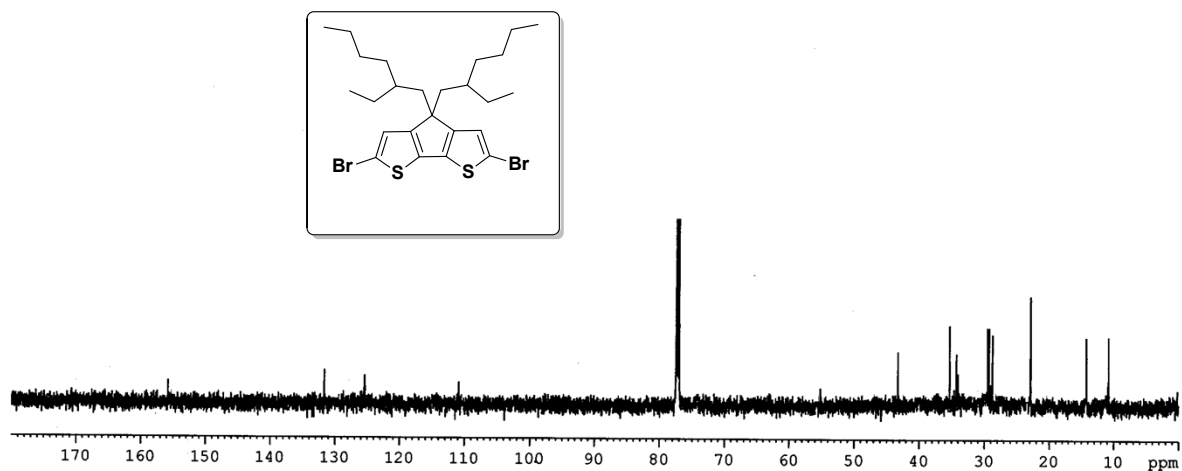


**Figure S33:** ESI-MS spectrum of 2,6-Dibromo-4,4'-bisdecyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1m).



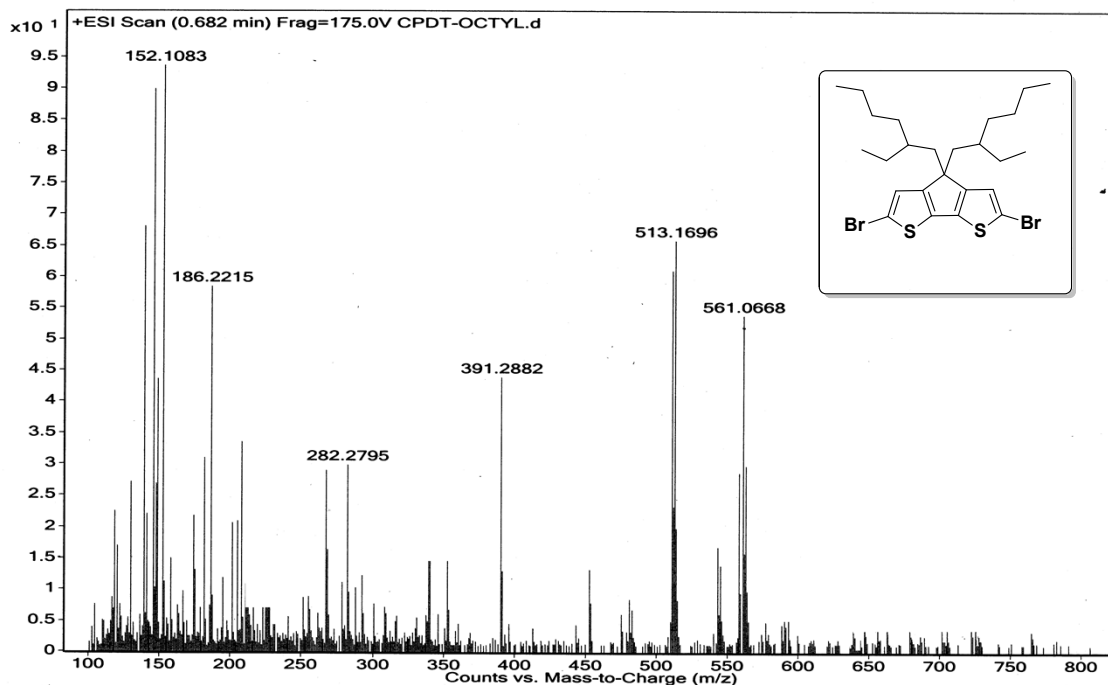
**Figure S34:** <sup>1</sup>H NMR spectrum of 2,6-Dibromo-4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1n).

TBR\_Br-CPDT-ET-19-13C

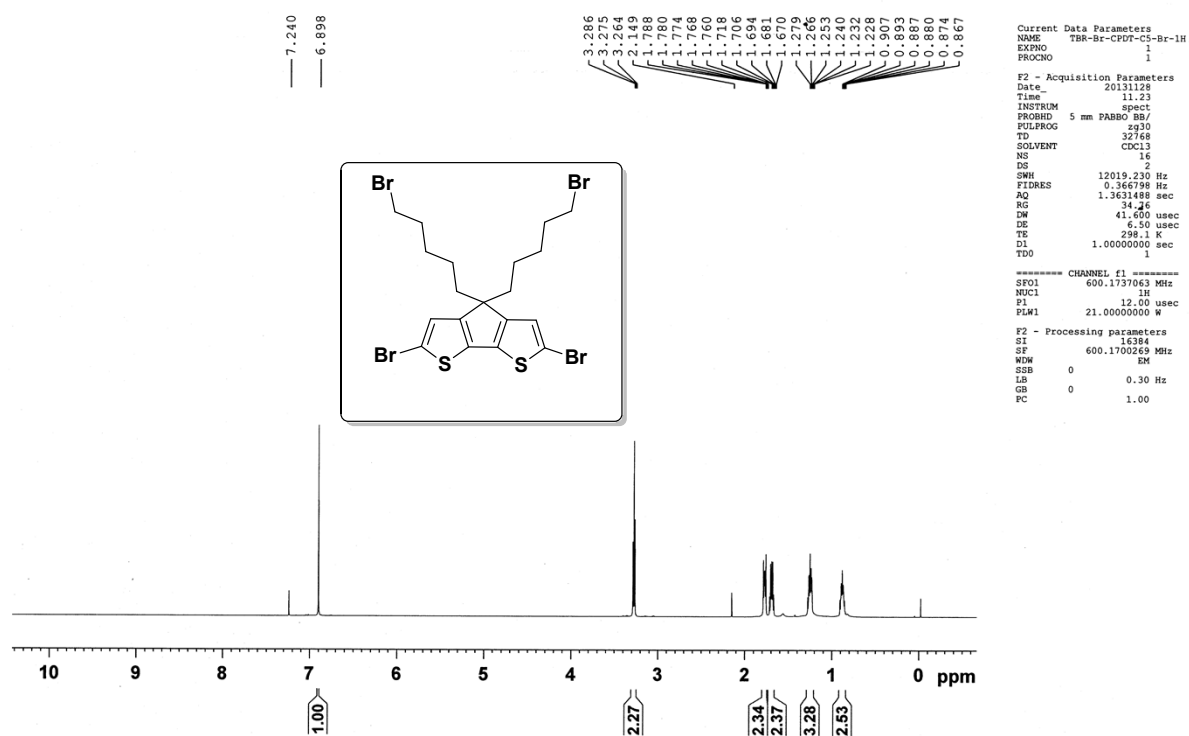


**Figure S35:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1n).

Sample Name	Br-CPDT-ET	Position	-1	Instrument Name	Instrument 1	User Name	
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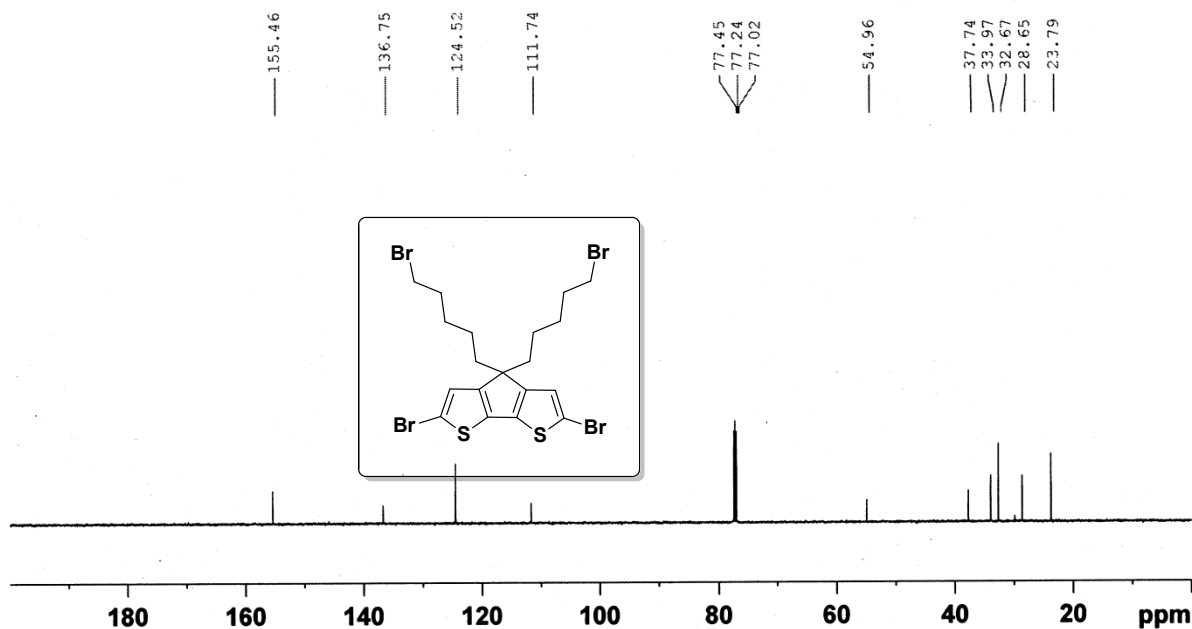


**Figure S36:** ESI-MS spectrum of 2,6-Dibromo-4,4'-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1n).



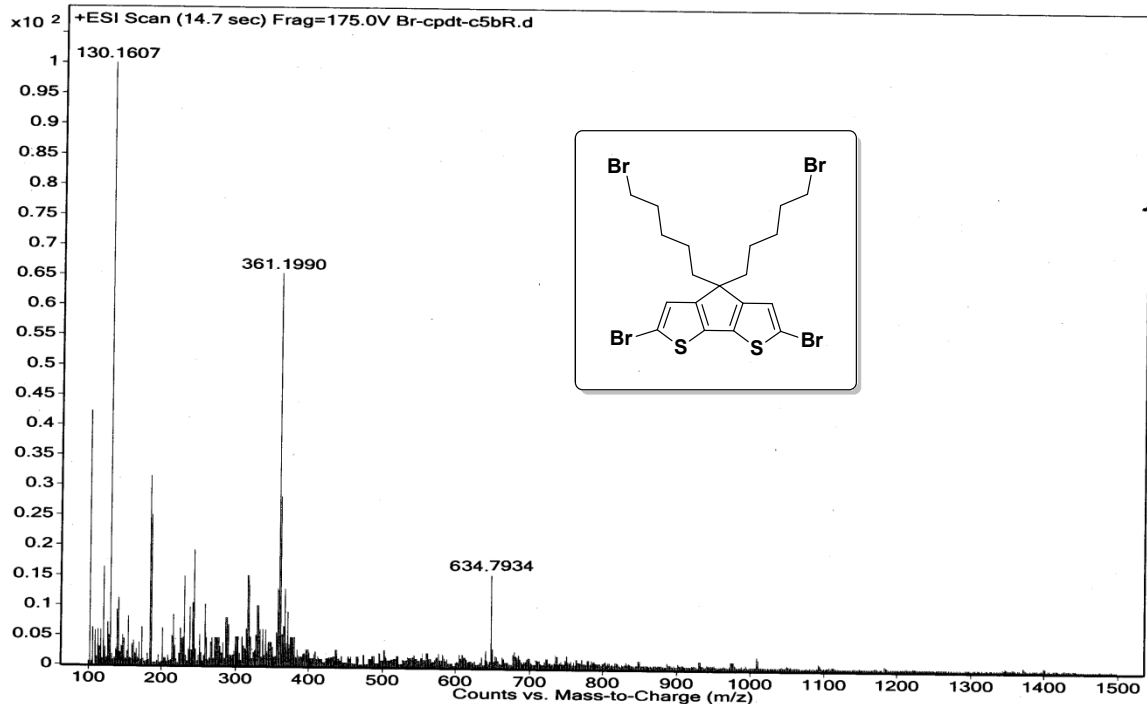
**Figure S37:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(5-bromopentyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1o).

Br\_CPDT\_C5\_Br\_13C

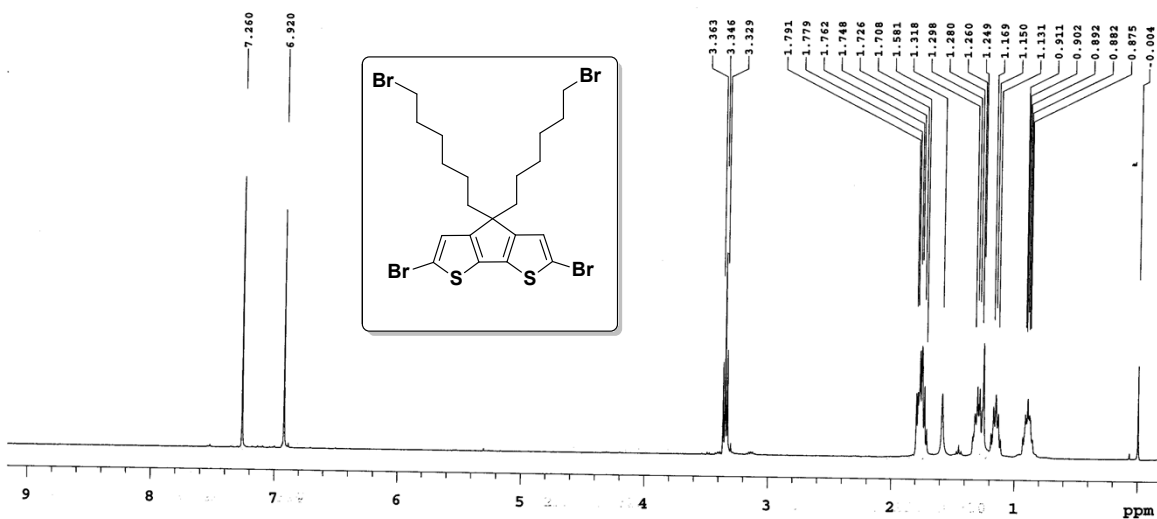


**Figure S38:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(5-bromopentyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1o).

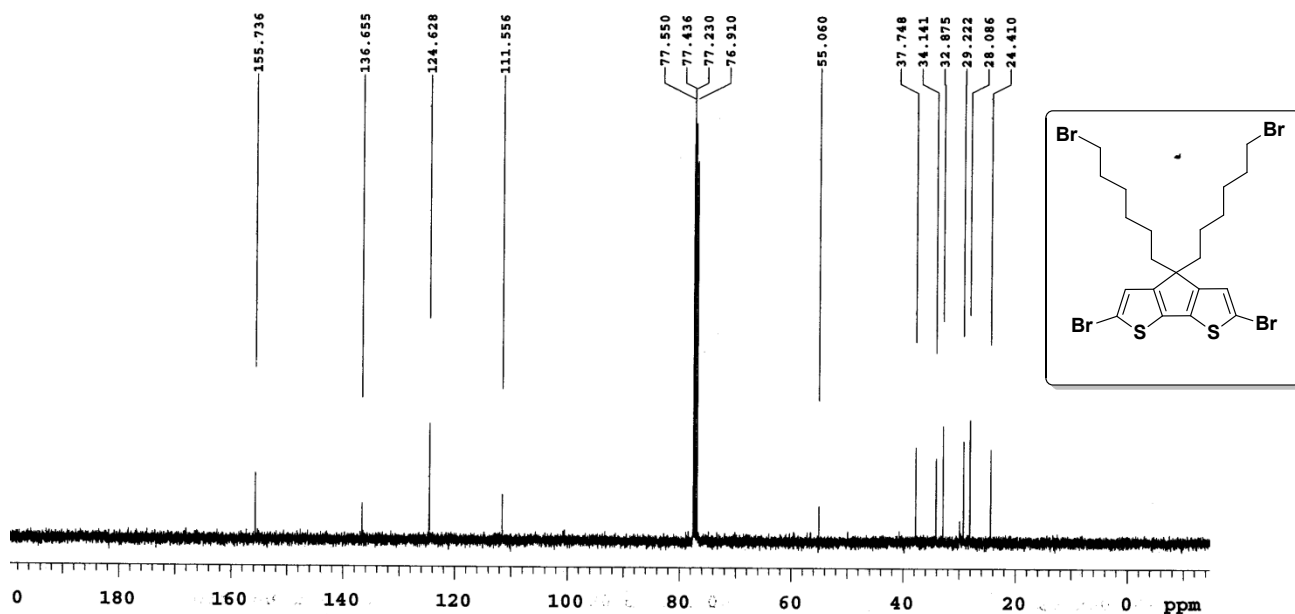
Sample Name	Br-cpdt-c5bR	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	Br-cpdt-c5bR.d	ACQ Method		Comment		Acquired Time	9/5/2013 10:59:38 AM



**Figure S39:** ESI-MS Spectrum of spectrum of 2,6-Dibromo-4,4'-bis(5-bromopentyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1o).

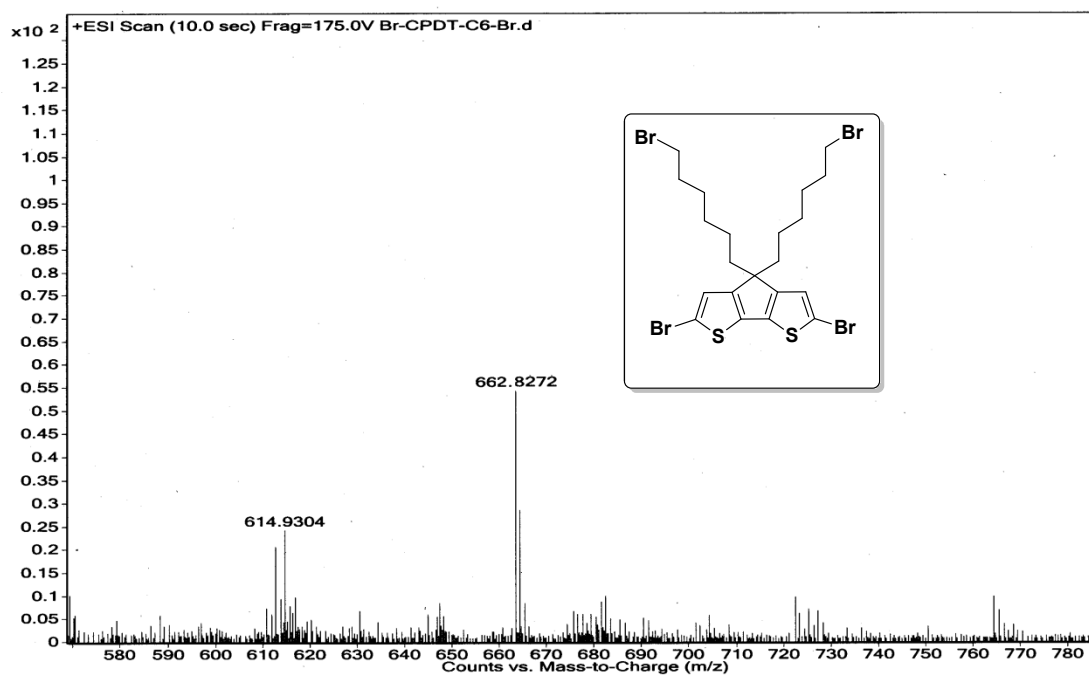


**Figure S40:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(6-bromohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1p).

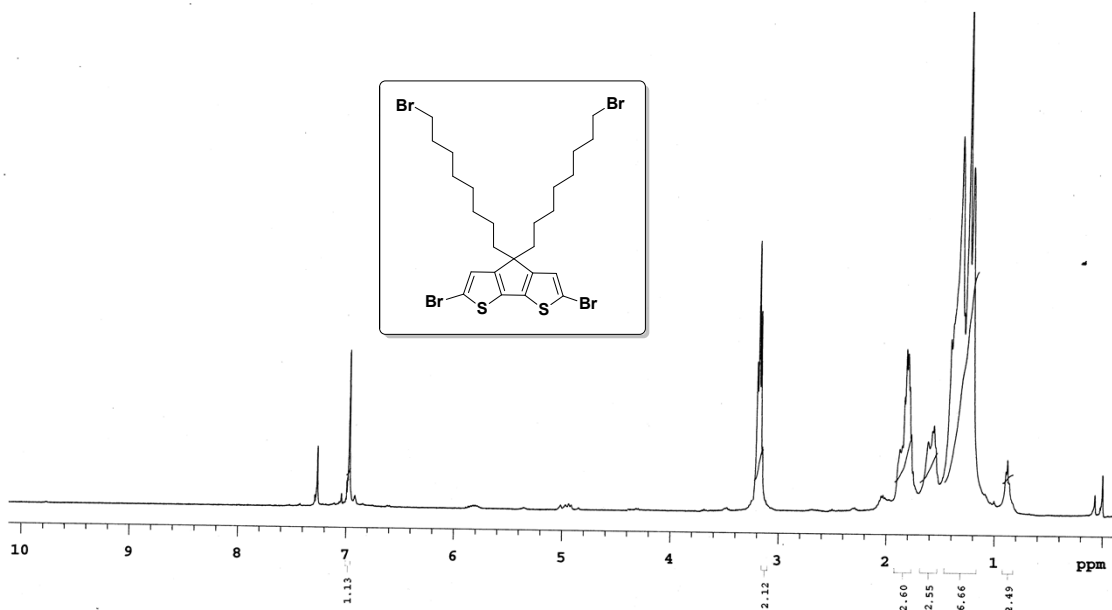


**Figure S41:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(6-bromohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1p).

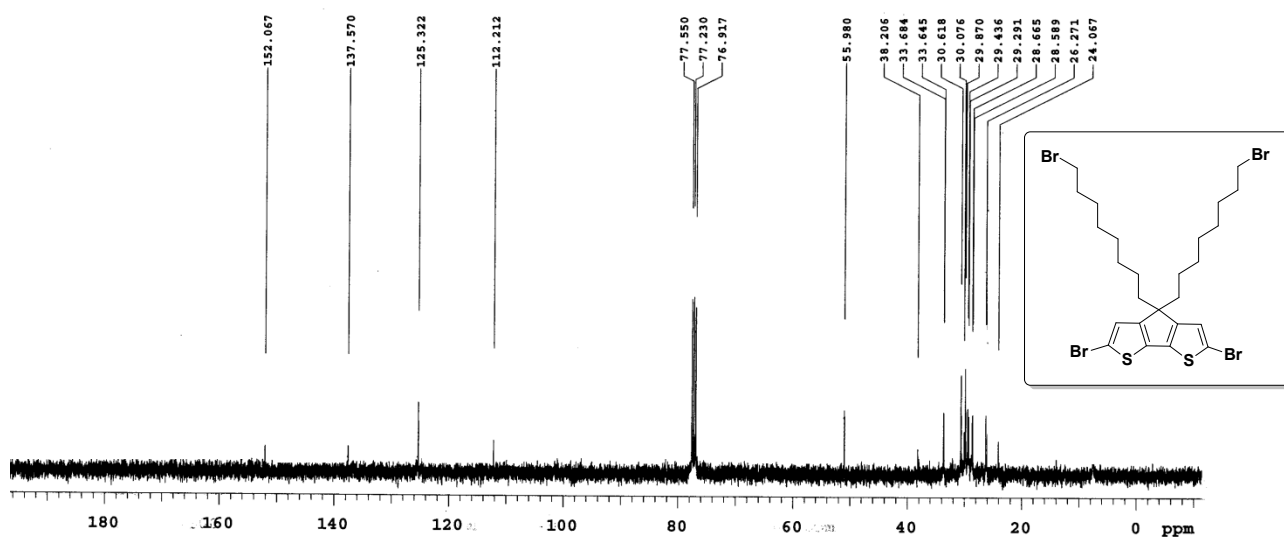
Sample Name	Br-CPDT-C6-Br	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	Br-CPDT-C6-Br.d	ACQ Method		Comment		Acquired Time	8/19/2013 11:01:36 AM



**Figure S42:** ESI-MS spectrum of 2,6-Dibromo-4,4'-bis(6-bromohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1p).

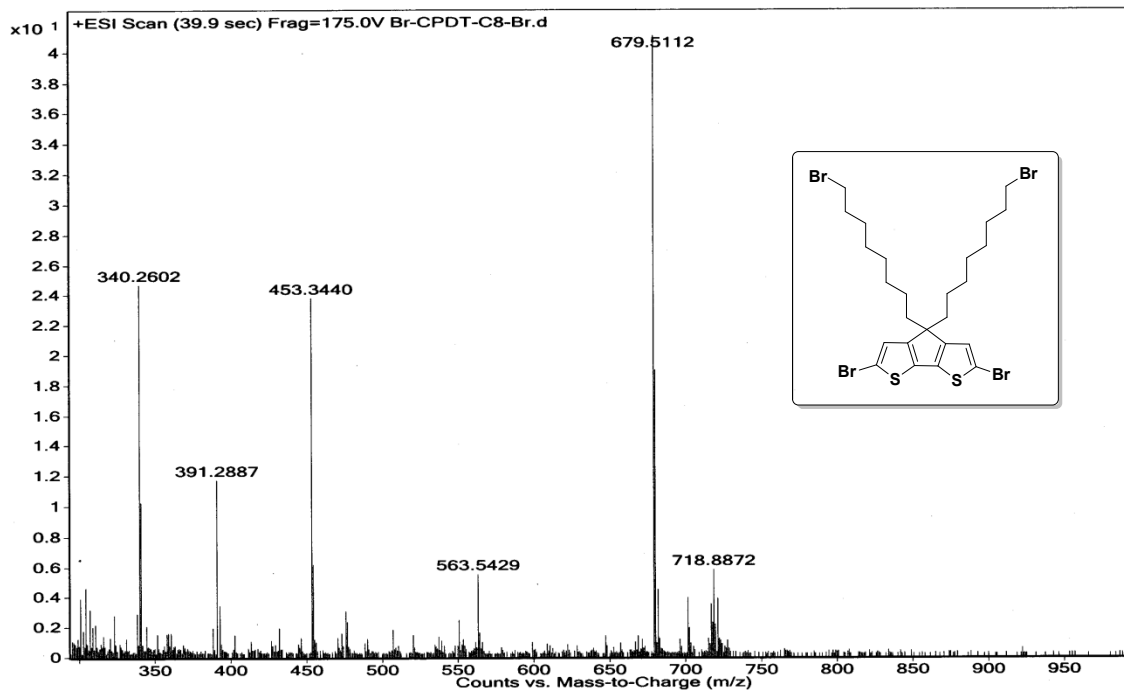


**Figure S43:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(8-bromooctyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1q).

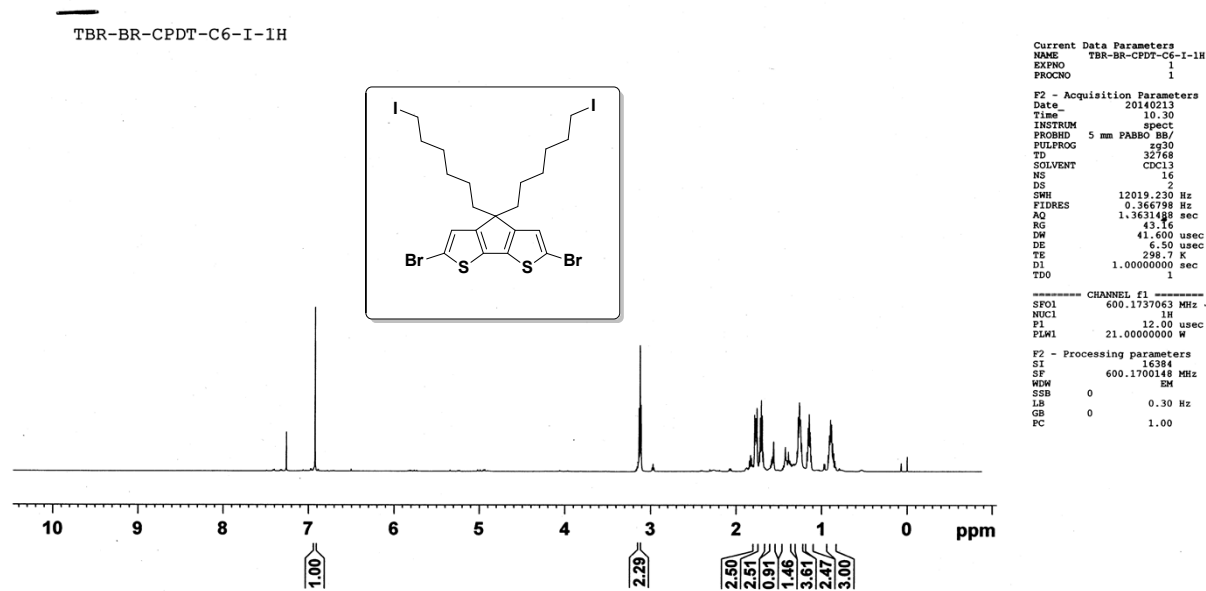


**Figure S44:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(8-bromooctyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1q).

Sample Name	Br-CPDT-C8-Br	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	Br-CPDT-C8-Br.d	ACQ Method		Comment		Acquired Time	8/19/2013 10:55:25 AM



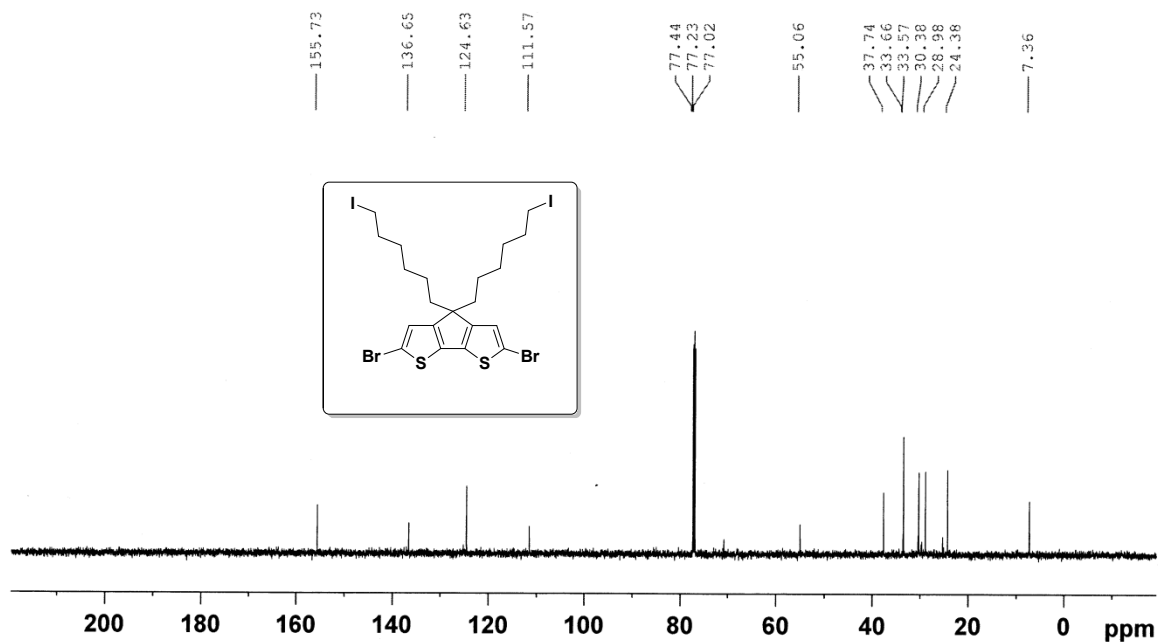
**Figure S45:** ESI-MS spectrum of 2,6-Dibromo-4,4'-bis(8-bromooctyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1q).



**Figure S46:**  $^1\text{H}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(6-iodohexyl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1r).

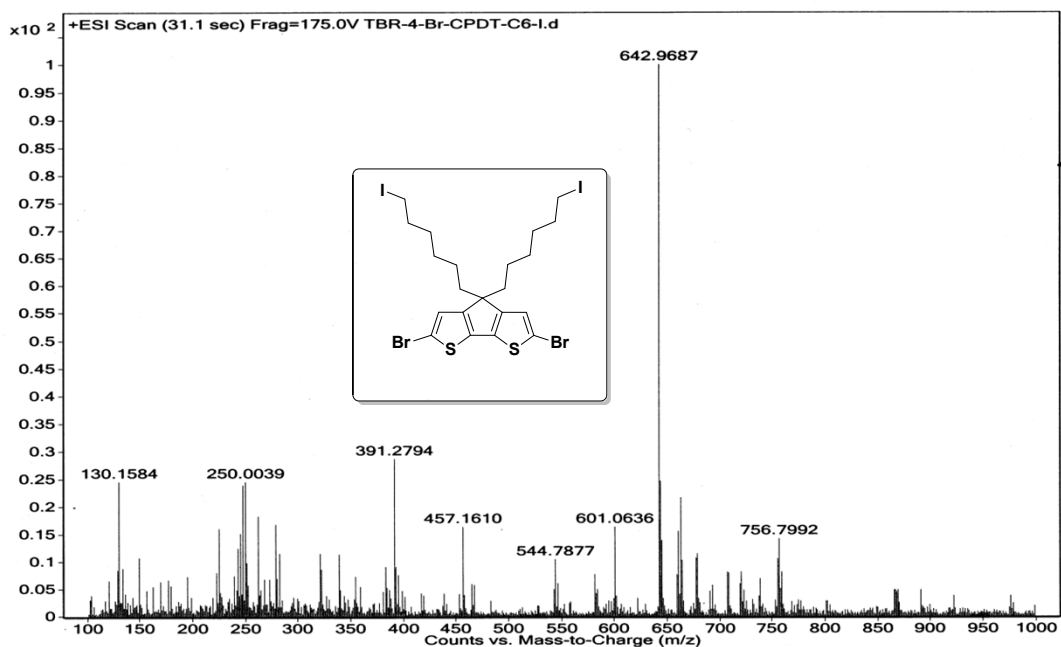


TBR-BR-CPDT-C6-I-13C

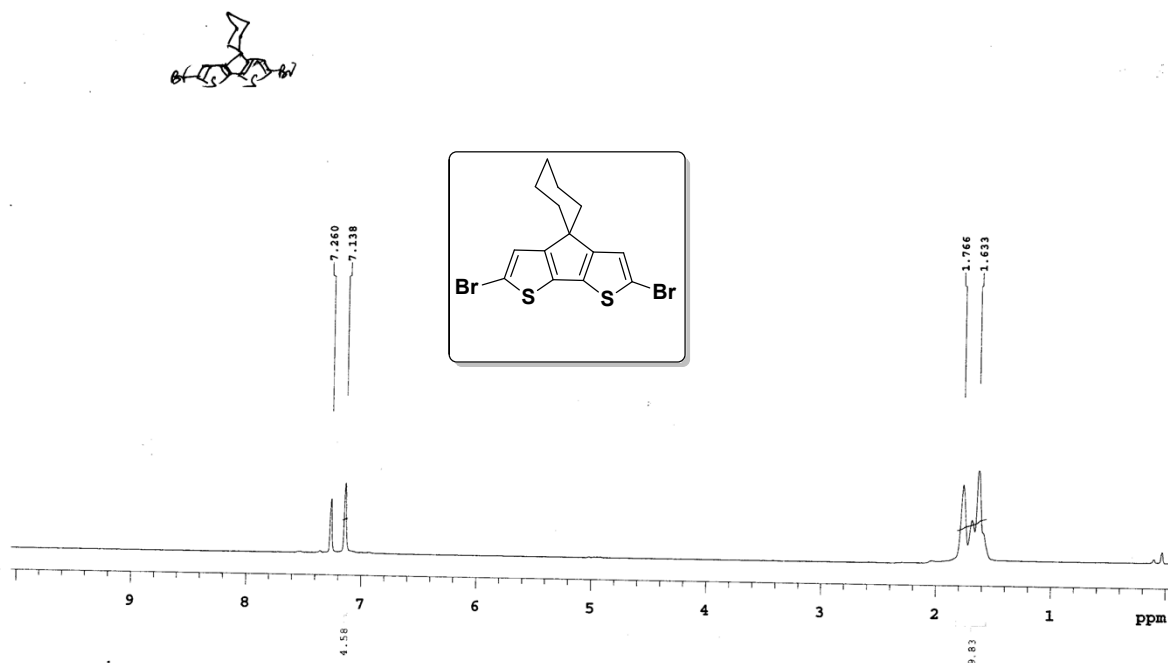


**Figure S47:**  $^{13}\text{C}$  NMR spectrum of 2,6-Dibromo-4,4'-bis(6-iodohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1r).

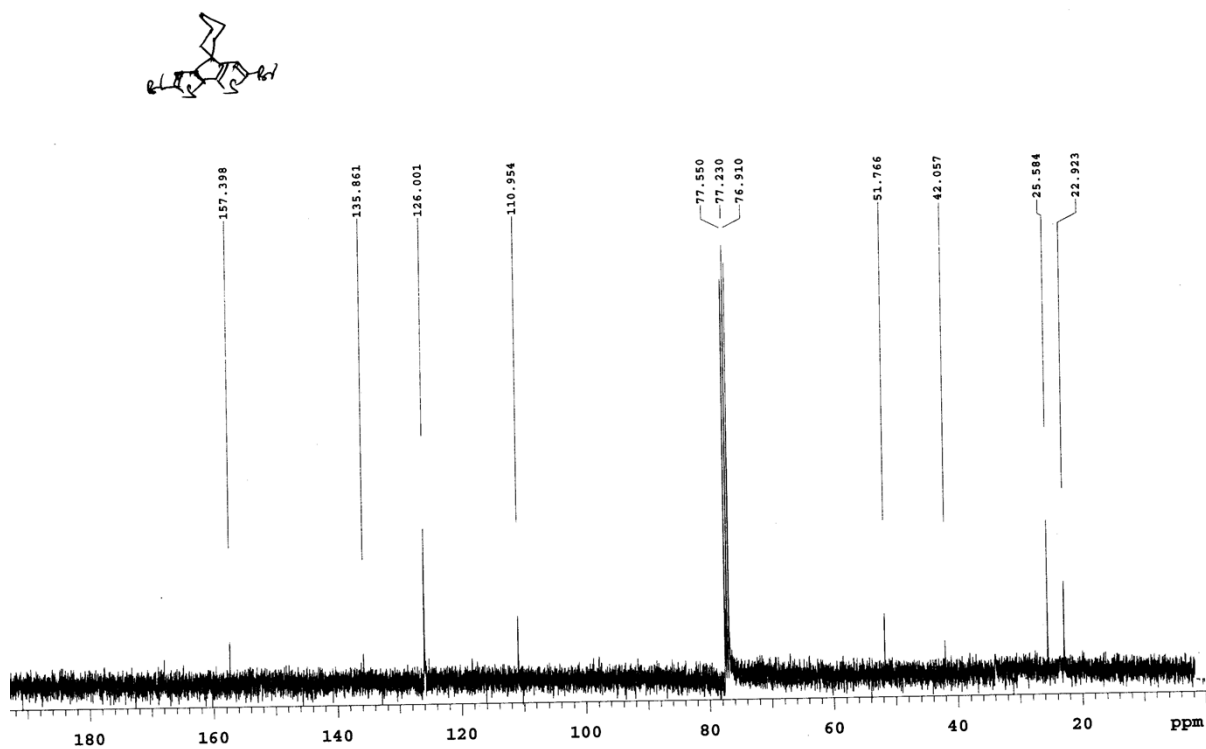
Sample Name	TBR-4-Br-CPDT-C6-I	Position	-1	Instrument Name	Instrument 1	User Name	
Inj Vol	-10	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	TBR-4-Br-CPDT-C6-I.d	ACQ Method		Comment		Acquired Time	3/4/2014 2:17:44 PM



**Figure S48:** ESI-MS spectrum of 2,6-Dibromo-4,4'-bis(6-iodohexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (entry 1r).

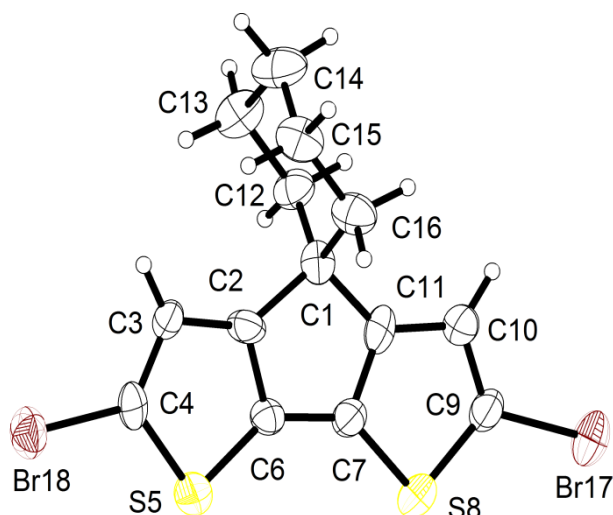


**Figure S49:** <sup>1</sup>H NMR spectrum of 2,6-Dibromo spiro[4,5] ([2,1-b; 3,4-b']dithieno)decane.



**Figure S50:** <sup>13</sup>C NMR spectrum of 2,6-Dibromo spiro[4,5] ([2,1-b; 3,4-b']dithieno)decane.

**Crystal Data**



**Figure S51.** ORTEP diagram of 2,6-Dibromo spiro[4,5] ([2,1-b; 3,4-b']dithieno)decane

**Crystal Data and Structure Refinement for TBr-Brcpdb-C5br at 296(2) K**

**Crystallographic parameters of 2,6-Dibromo spiro[4,5] ([2,1-b; 3,4-b']dithieno)decane**

Compound	TBr-Brcpdb-C5br
Formula	C <sub>14</sub> H <sub>12</sub> Br <sub>2</sub> S <sub>2</sub>
CCDC NO	1005162
Formula. wt.	404.18
Crystal system	Monoclinic
Space group	P 21/c
<i>a</i> (Å)	6.5657(4)
<i>b</i> (Å)	15.4051(8)
<i>c</i> (Å)	14.3212(7)
α(°)	90
β(°)	100.183(5)
γ(°)	90
V/ Å <sup>3</sup>	1425.71(14)
Z	4
Density/Mgm <sup>-3</sup>	1.883
Abs. Coeff/mm <sup>-1</sup>	5.957
F(000)	792
Total no. of reflections	5206
Reflections, <i>I</i> > 2σ( <i>I</i> )	1578
Max. 2θ/°	6.02 to 57.2°
Ranges (h, k, l)	-7 ≤ h ≤ 7, -16 ≤ k ≤ 18, -16 ≤ l ≤ 17
Complete to 2θ (%)	1.00
Data/ Restraints/Parameters	2507/0/163
Goof ( <i>F</i> <sub>2</sub> )	1.026

R indices [ $I \geq 2\sigma(I)$ ]	0.0631
R indices (all data)	0.1046