

Electronic Supplementary Information

Dithieno[3,2-*b*:2',3'-*d*]pyrrole based, NIR absorbing, solution processable, small molecule donor for efficient bulk heterojunction solar cells.

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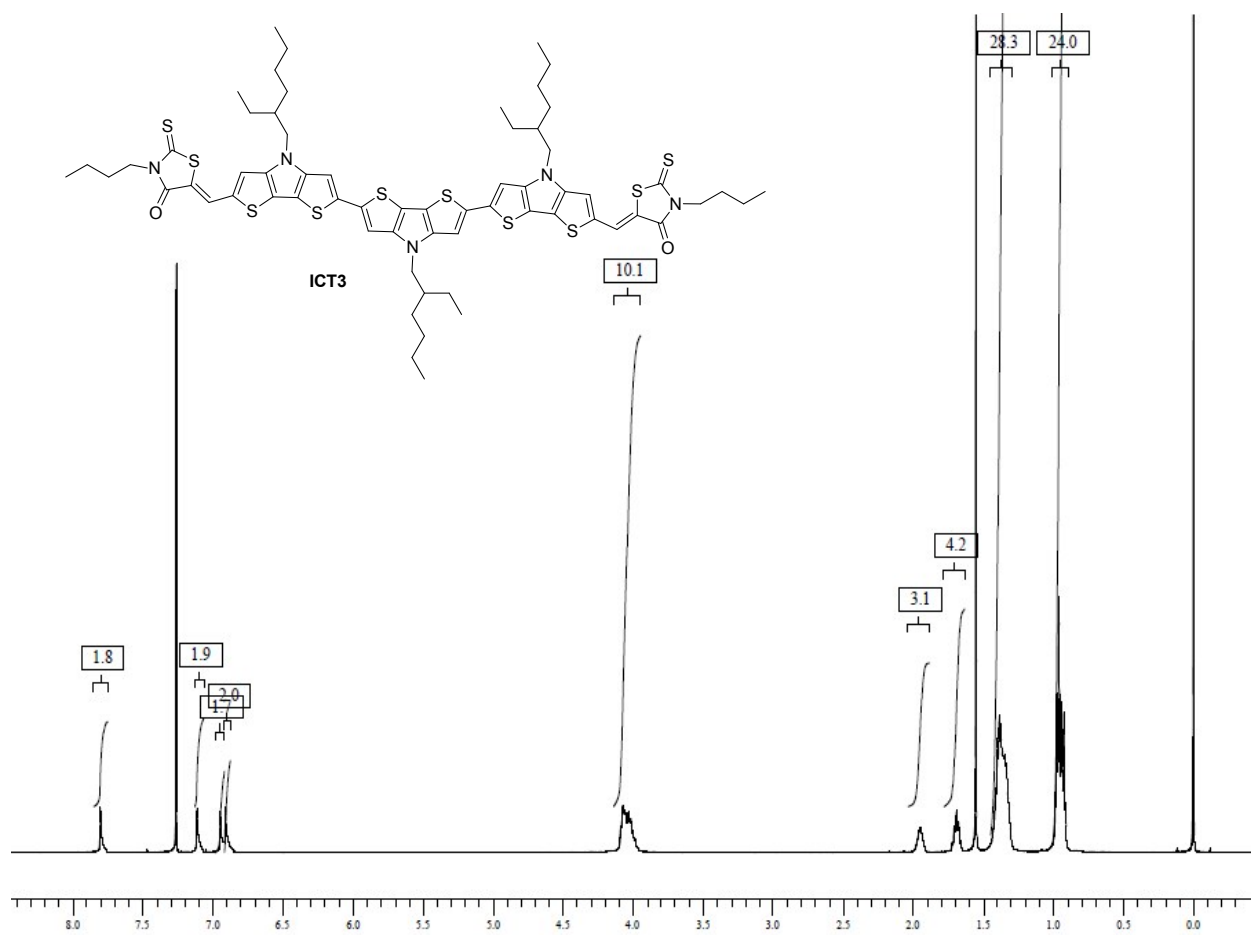


Fig. S1. ¹H NMR spectrum of ICT3

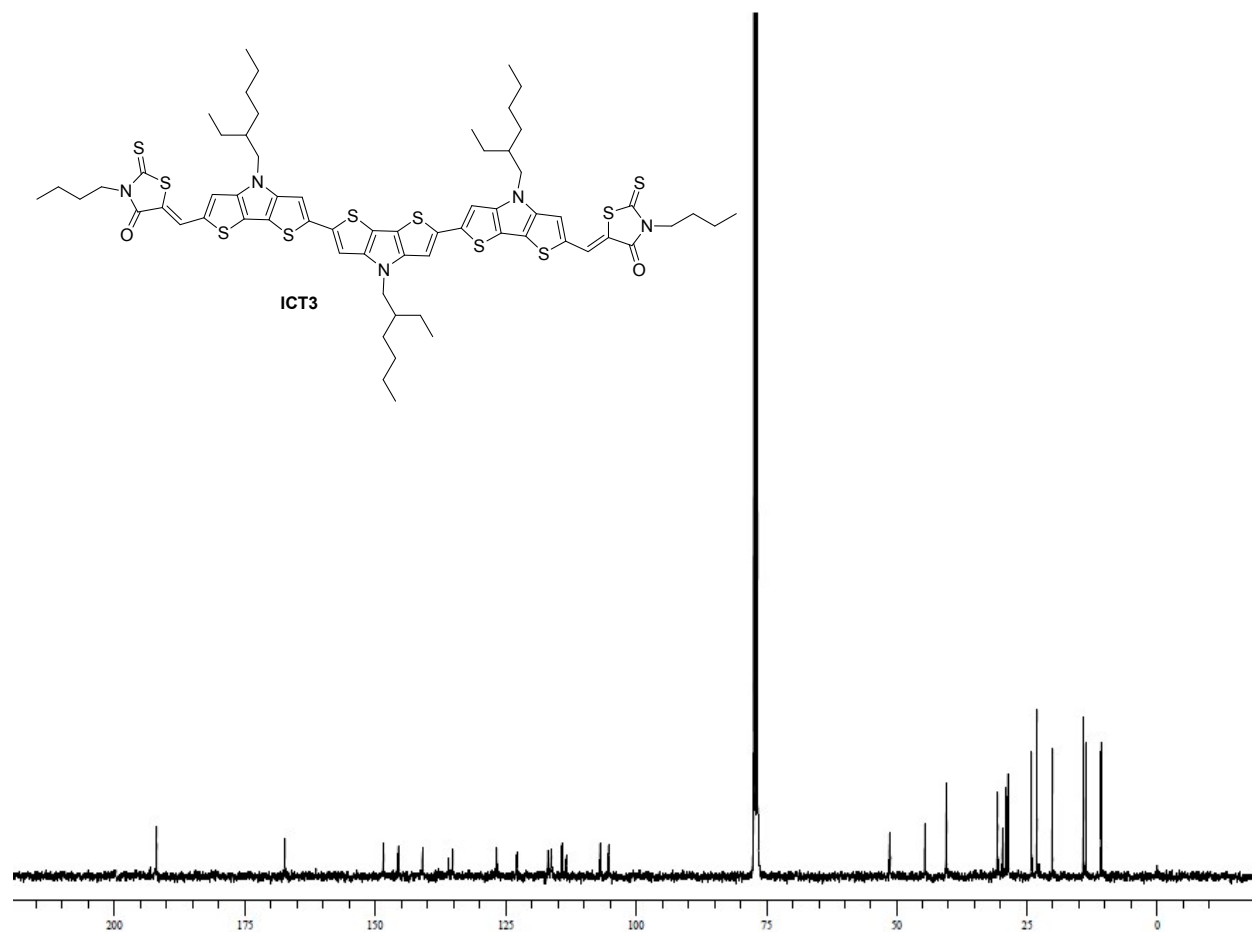


Fig. S2. ¹³C NMR spectrum of ICT3

M V N RAJU , MNR-NF

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Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 69, Blanked, P.Ext. @ 2000 (bin 66)
%Int. 105 mV[sum= 2737 mV] Profiles 1-26 Smooth Gauss 5

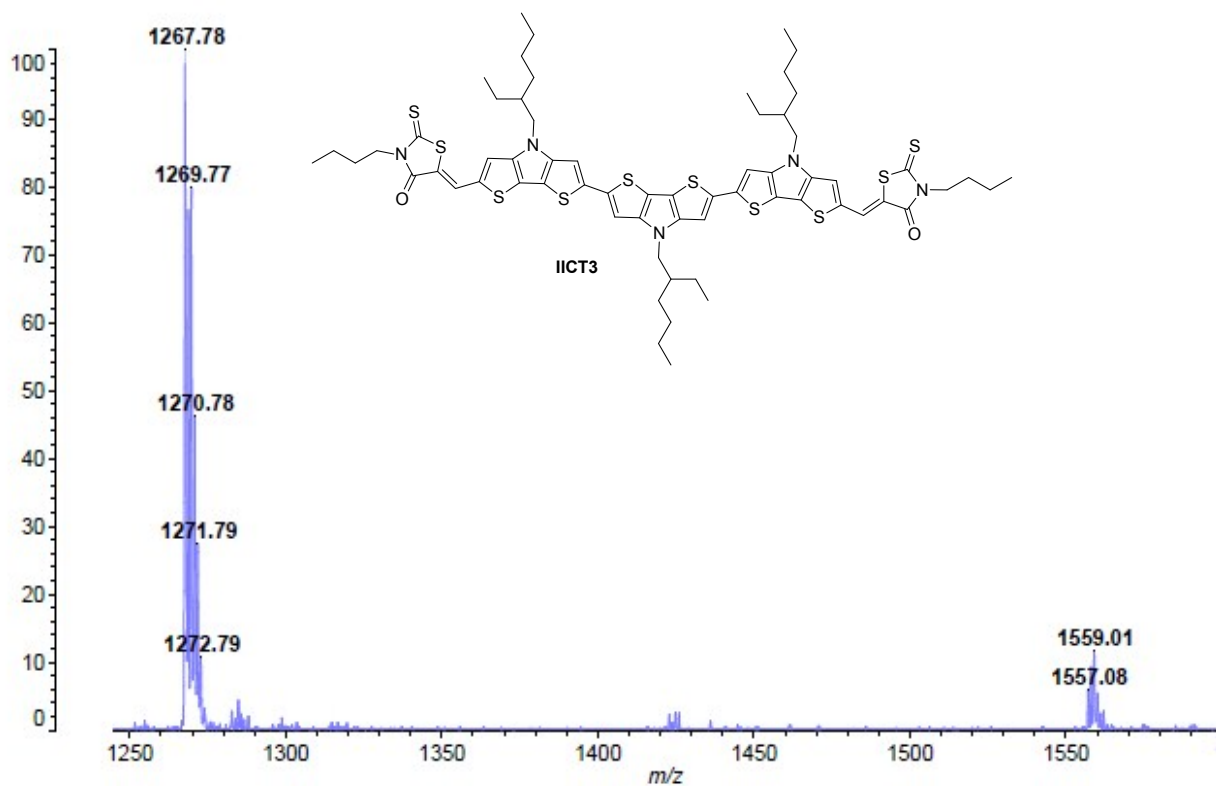
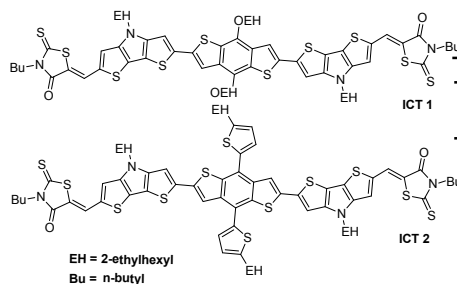


Fig. S3. MALDI-MS spectrum of ICT3

Material Code	λ_{\max} (nm) ^a	ξ ($\times 10^5 \text{ mol}^{-1} \text{ cm}^{-1}$) ^a	λ_{\max} (nm) ^b	$E_{\text{o-o}}$ (eV) ^c	$E_{\text{g}}^{\text{opt}}$ (eV) ^d	E_{ox} (V)	E_{HOMO} (eV)	E_{LUMO} (eV) ^e
ICT1	586	1.71	604	1.96	1.68	0.29	-5.39	-3.43
ICT2	594	1.65	608	2.02	1.63	0.38	-5.48	-3.46

Active layer	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)	R_{s} ($\Omega \text{ cm}^2$)	R_{sh} ($\Omega \text{ cm}^2$)
ICT1:PC ₇₁ BM (as cast)	6.84	0.92	0.44	2.77	24.06	510
ICT2:PC ₇₁ BM (as cast)	7.26	0.96	0.47	3.27	22.16	564
ICT1:PC ₇₁ BM (TSA)	10.15	0.87	0.58	5.12	12.92	686
ICT2:PC ₇₁ BM (TSA)	10.68	0.92	0.60	5.90	9.08	746



^ain dilute chloroform solution (10 μM), ^bin thin film cast from chloroform solution, ^cestimated from intersection of absorption and emission spectra in chloroform solution, ^destimated from $E_{\text{g}}^{\text{opt}}=1240/\lambda_{\text{onset}}$, λ_{onset} is onset absorption wavelength in thin film, ^e $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{o-o}}$.

Fig. S4. Chemical structures of ICT1 and ICT2 and their photophysical, electrochemical and photovoltaic data

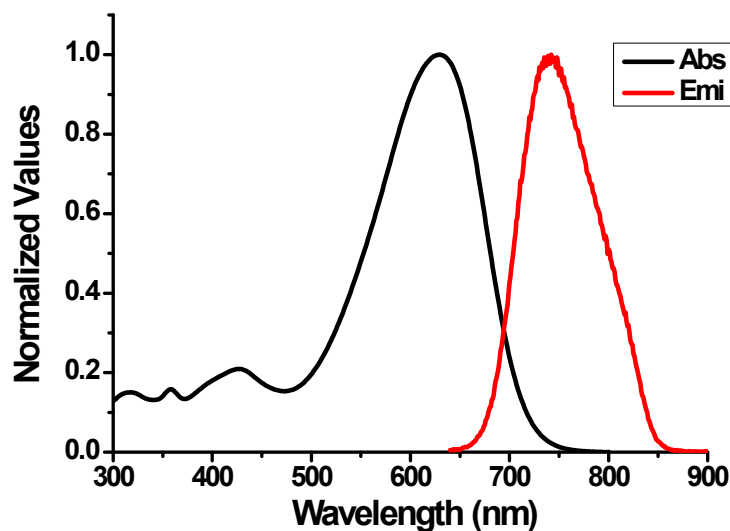


Fig. S5. Absorption and fluorescence spectra of ICT3 (10 μM) measured in chloroform solution.

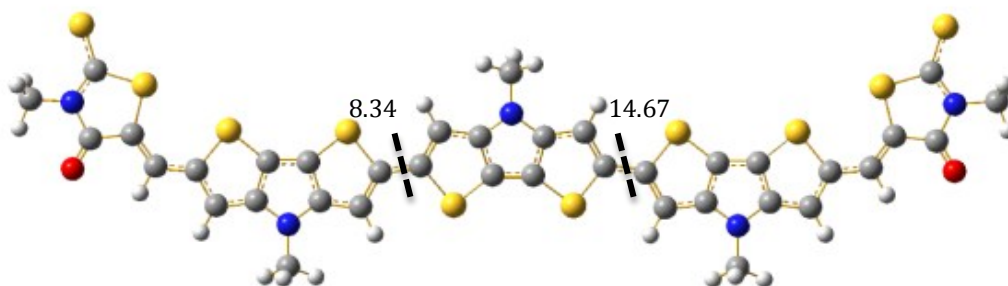


Fig. S6. Optimized structure of ICT3.

Table S1 Calculated properties of ICT3 at M06/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength f , the wavelength maxima, the major contribution (%) to the first excited state and the dipole moment μ_g (D).^a

Molecule	HOMO (eV)	LUMO (eV)	HLG (eV)	λ (nm)	OG (eV)	f	Major contribution (%)	μ_g^a (D)
ICT3	-5.1	-2.69	2.41	628	1.974	3.520	H -1 \rightarrow L+1 (4%) H \rightarrow L (95%)	9.07
	<i>-5.04</i>	<i>-2.71</i>	<i>2.33</i>	<i>676</i>	<i>1.834</i>	<i>3.707</i>	<i>H -1 \rightarrow L+1 (4%) H \rightarrow L (93%)</i>	<i>12.27</i>

^a values given in *Italic font* are the values obtained in the solvent phase CF.

Table S2 Calculated properties of ICT3 at B3LYP/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength f , the wavelength maxima, the major contribution (%) to the first excited state and the dipole moment μ_g (D).^a

Molecule	HOMO (eV)	LUMO (eV)	HLG (eV)	λ (nm)	OG	f	Major contribution (%)	μ_g^b (D)
ICT3	-4.82	-2.76	2.06	664	1.867	3.291	H \rightarrow L (99%)	9.72
	<i>-4.75</i>	<i>-2.76</i>	<i>1.97</i>	<i>724</i>	<i>1.712</i>	<i>3.484</i>	<i>H \rightarrow L (98%)</i>	<i>13.15</i>

^a values given in *Italic font* are the values obtained in the solvent phase CF.

Table S3 Calculated properties of ICT3 at PBE/6-31G(d,p) level. HOMO and LUMO energies (eV), HOMO–LUMO gap HLG (eV), Optical gap OG (eV), oscillator strength f , the wavelength maxima, the major contribution (%) to the first excited state and the dipole moment μ_g (D).^a

Molecule	HOMO (eV)	LUMO (eV)	HLG (eV)	λ (nm)	OG (eV)	f	Major contribution (%)	μ_g (D)
ICT3	-4.82	-2.76	2.06	839	1.4770	1.975	H -1 \rightarrow L+1 (6%) H \rightarrow L+2 (3%) H \rightarrow L (91%)	9.70

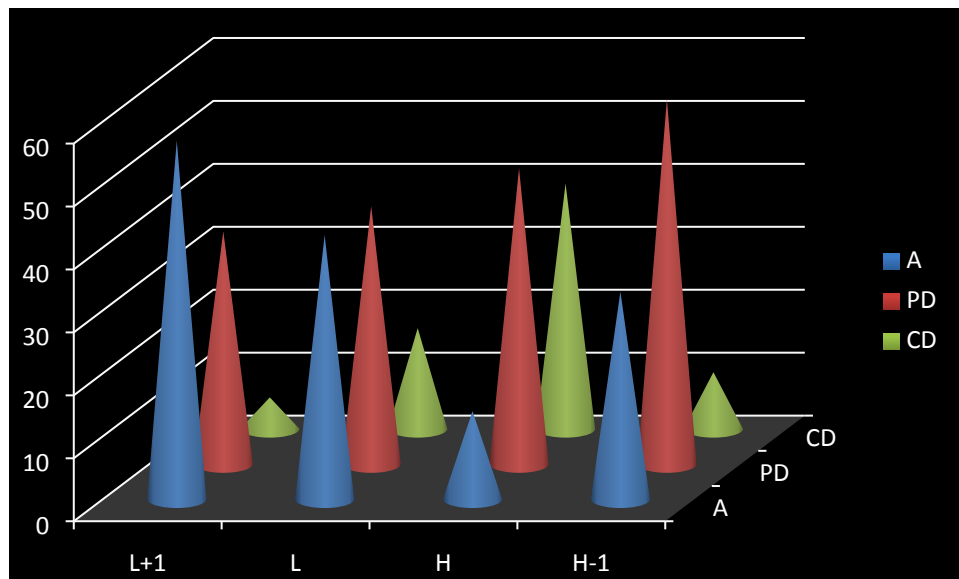


Fig. S7. Graphical representation of percentage contribution of different moieties of ICT3.

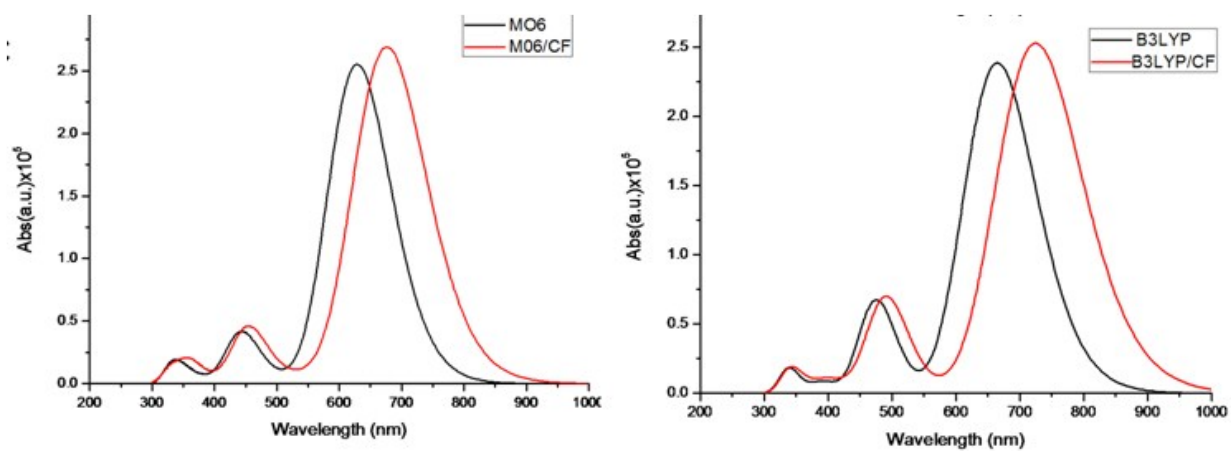


Fig. S8. Simulated UV-Vis Absorption spectra of ICT3 using M06 and B3LYP in gas phase and solvent chloroform (CF)

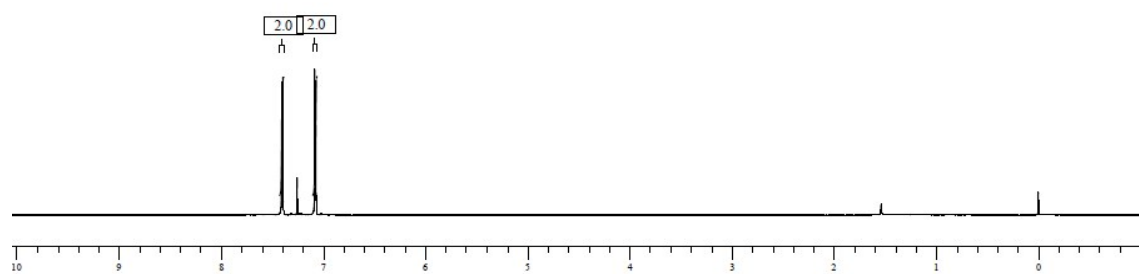
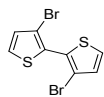


Fig. S9. ¹H NMR spectrum of **1**

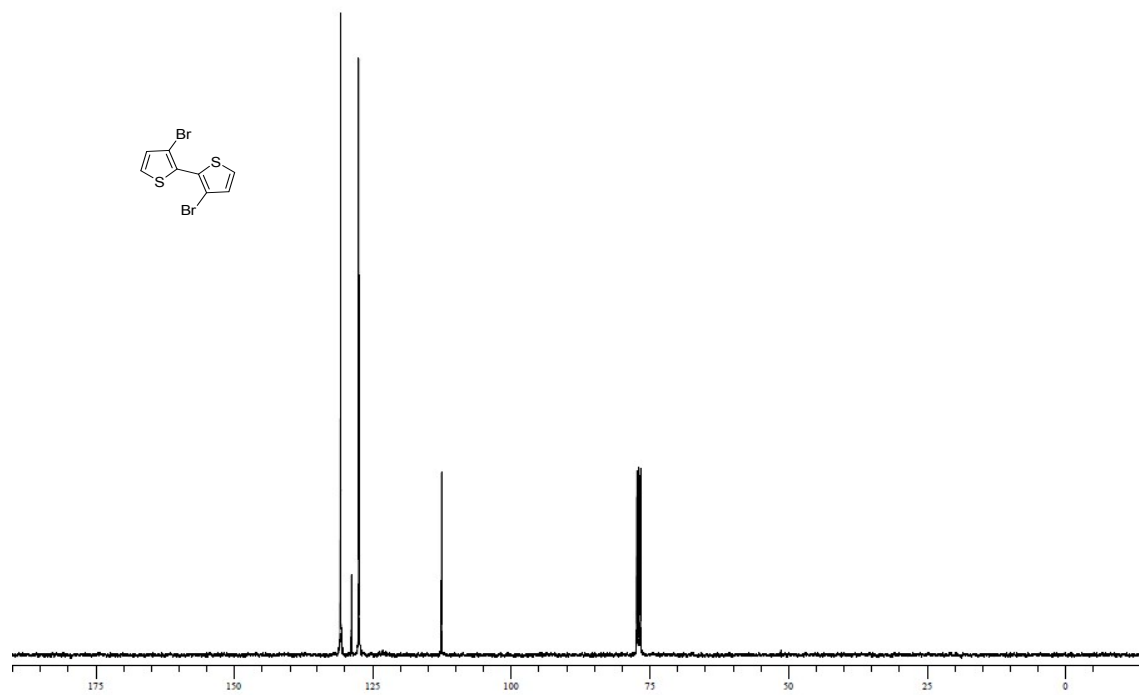


Fig. S10. ¹³C NMR spectrum of **1**

Acq. Data Name: JRAO-MR-BRBT
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Comment: JRAO-MR-BRBT, EIHRMS ,DIP-300

Experiment Date/Time: 08-09-2016 17:47:56
Ionization Mode: EI+

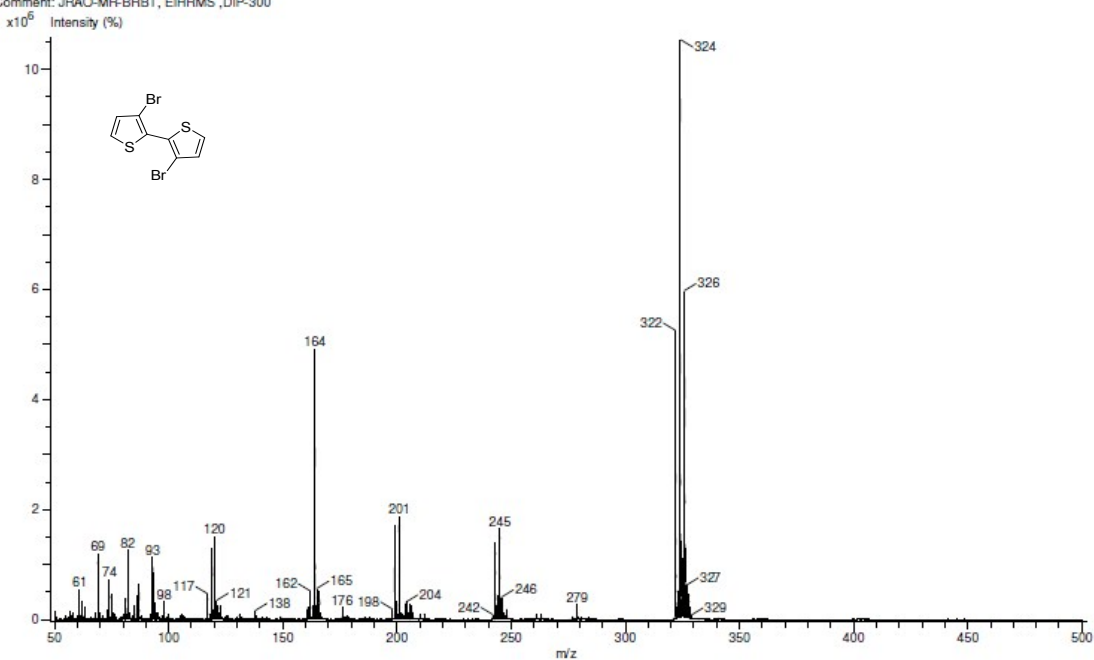


Fig. S11. EI-MS spectrum of 1

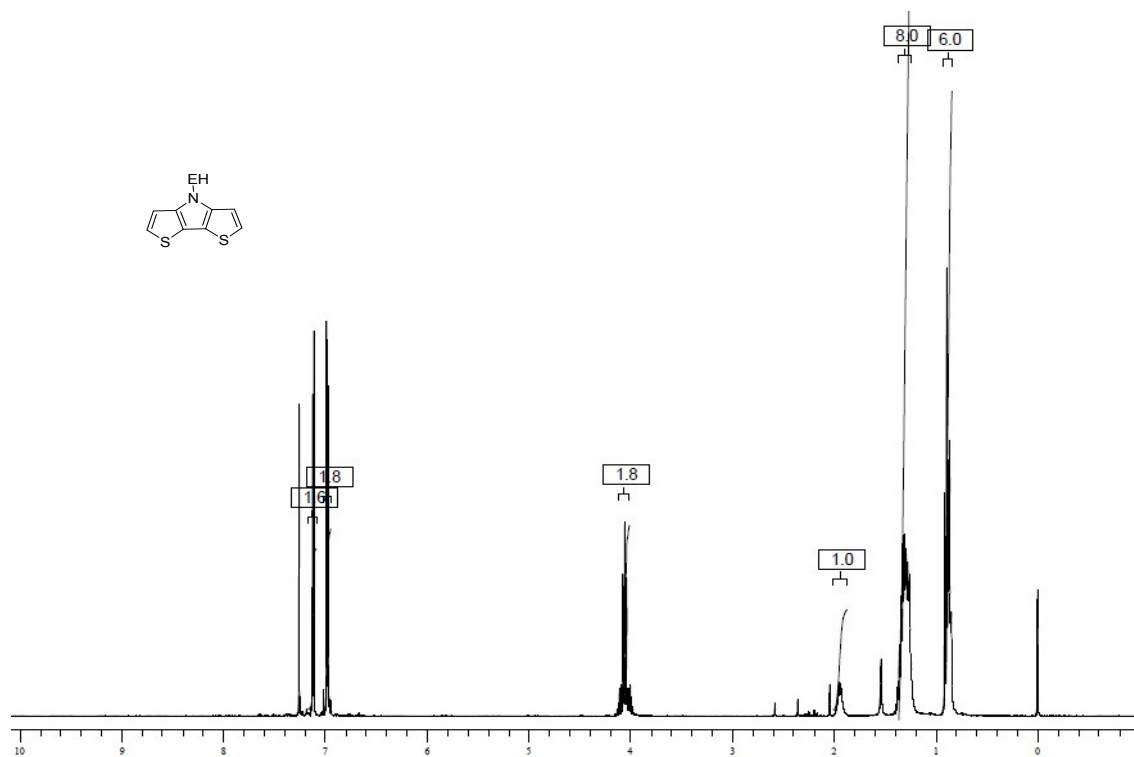


Fig. S12. ¹H NMR spectrum of 2

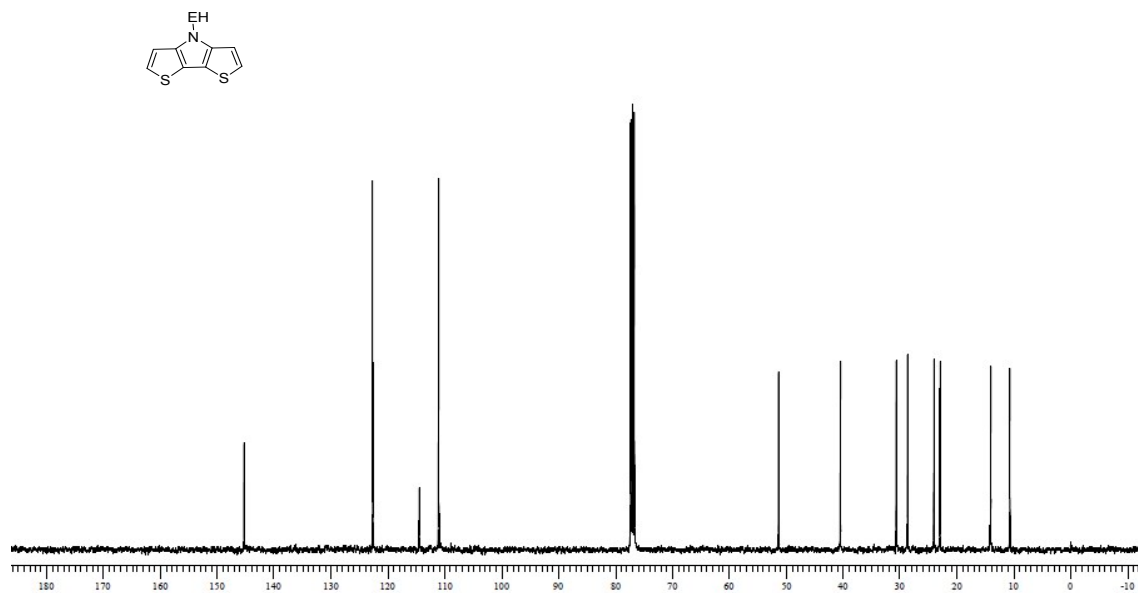


Fig. S13. ^{13}C NMR spectrum of **2**

=== CPC DIVISION @ CSIR-IICT ===

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 Sample ID : IRAD-MR-DTP
 Original Data File : D:\LCMS\Data\ESI-APCI Mass\2016\02-09-2016\IRAD-MR-DTP.fid

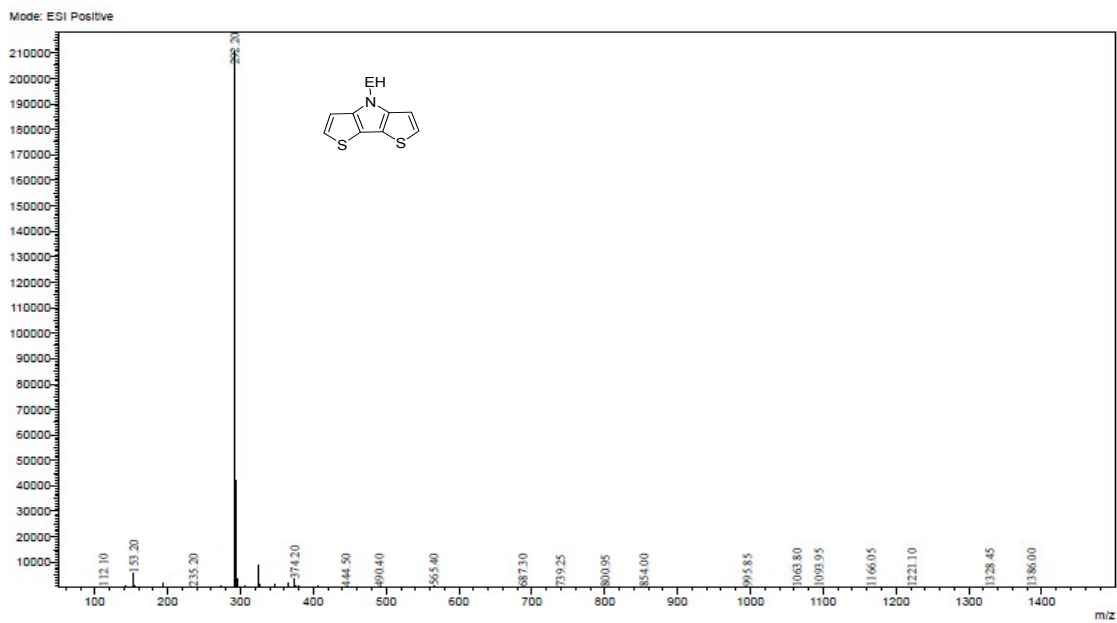


Fig. S14. ESI-MS spectrum of **2**

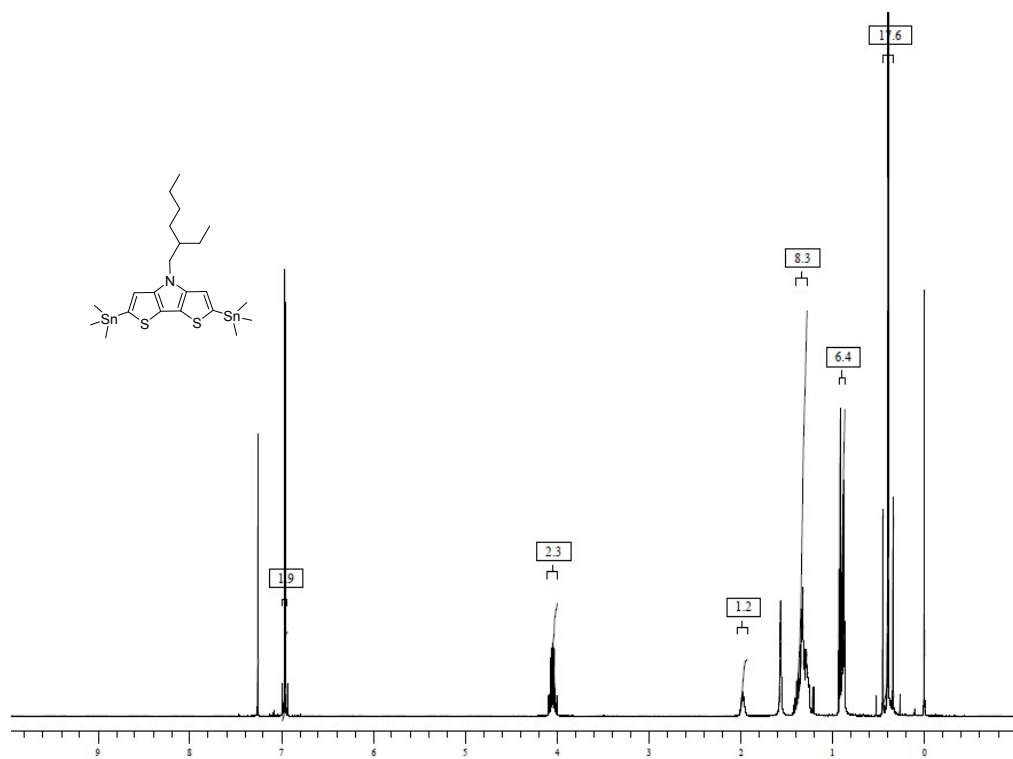


Fig. S15. ¹H NMR spectrum of **3**

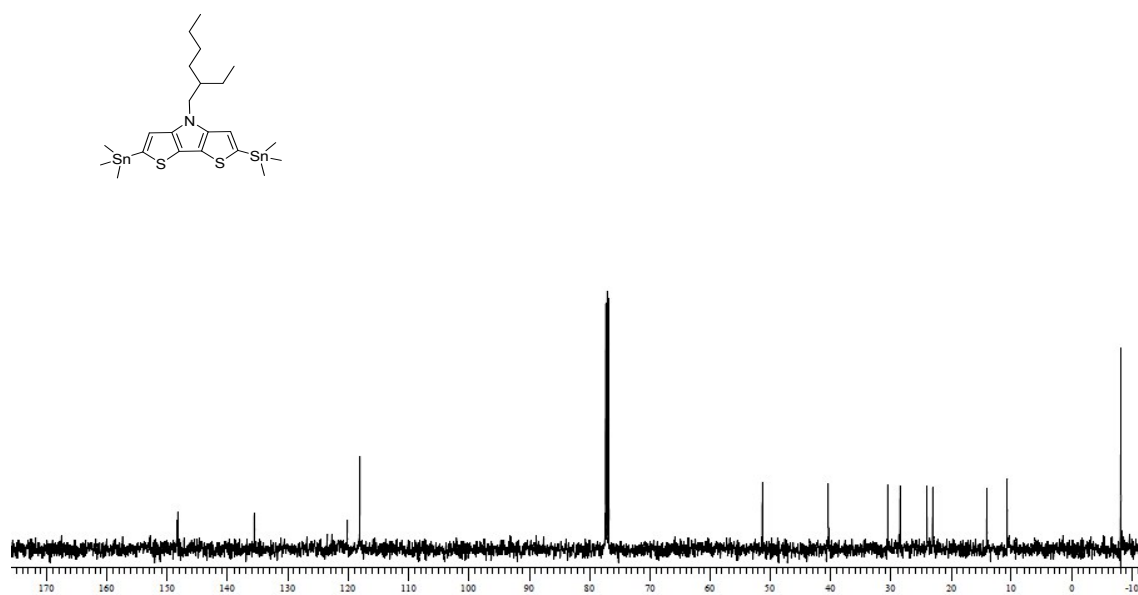


Fig. S16. ¹³C NMR spectrum of **3**

Acq. Data Name: JRAO-MR-DTPS
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 Comment: JRAO-MR-DTPS, EIHRMS_DIP-300

Experiment Date/Time: 08-09-2016 17:52:15
 Ionization Mode: EI+

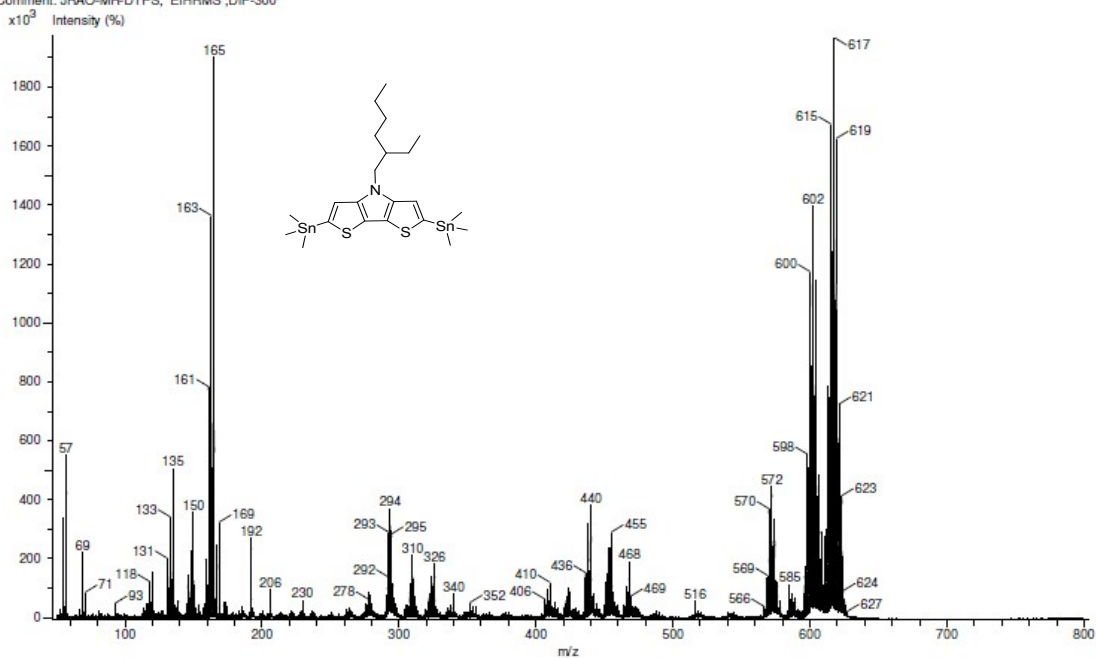


Fig. S17. EI-MS spectrum of 3

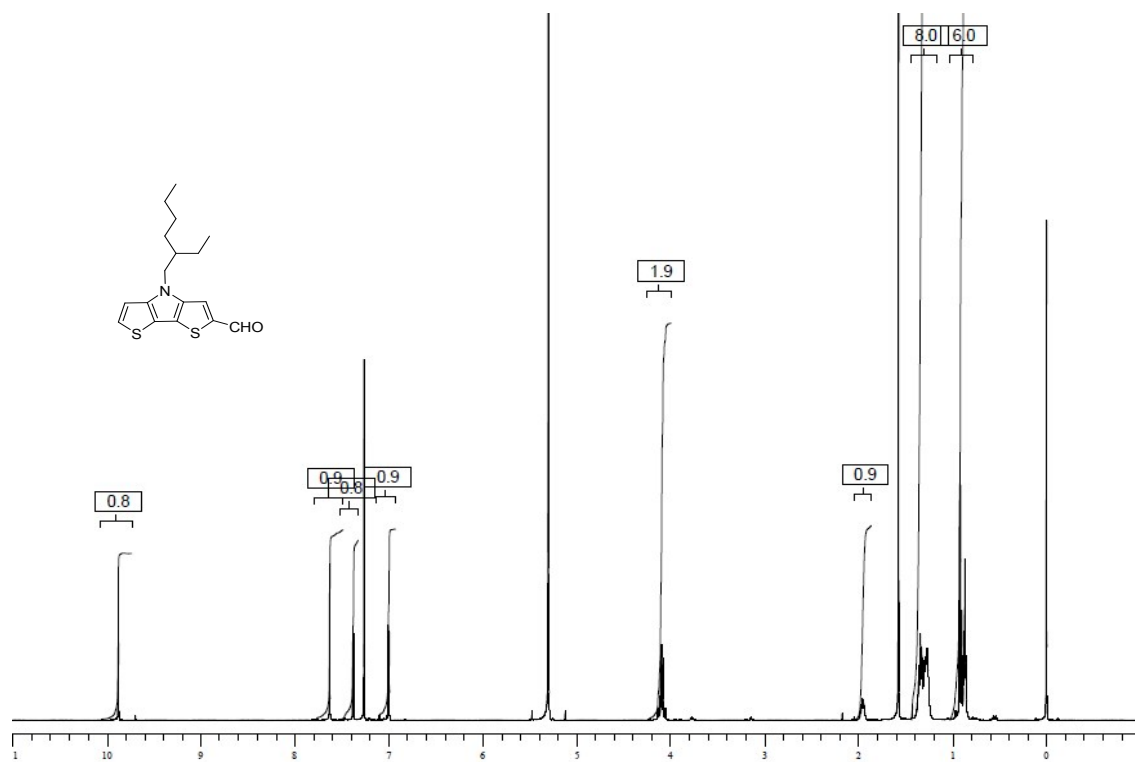


Fig. S18. ¹H NMR spectrum of 4

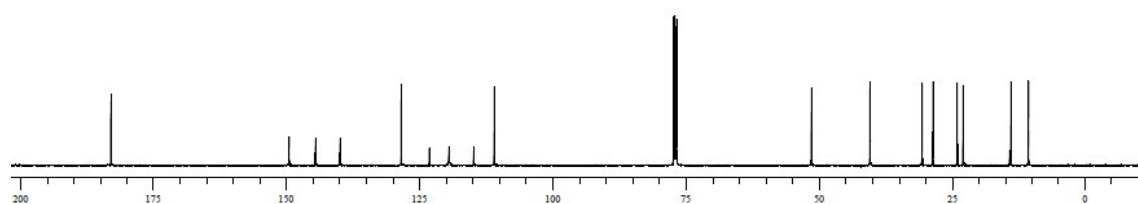
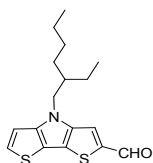


Fig. S19. ¹³C NMR spectrum of 4

=== CPC DIVISION @ CSIR-IICT ===

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 Sample ID : JRAO-MR-DTPA
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Mode: ESI Positive

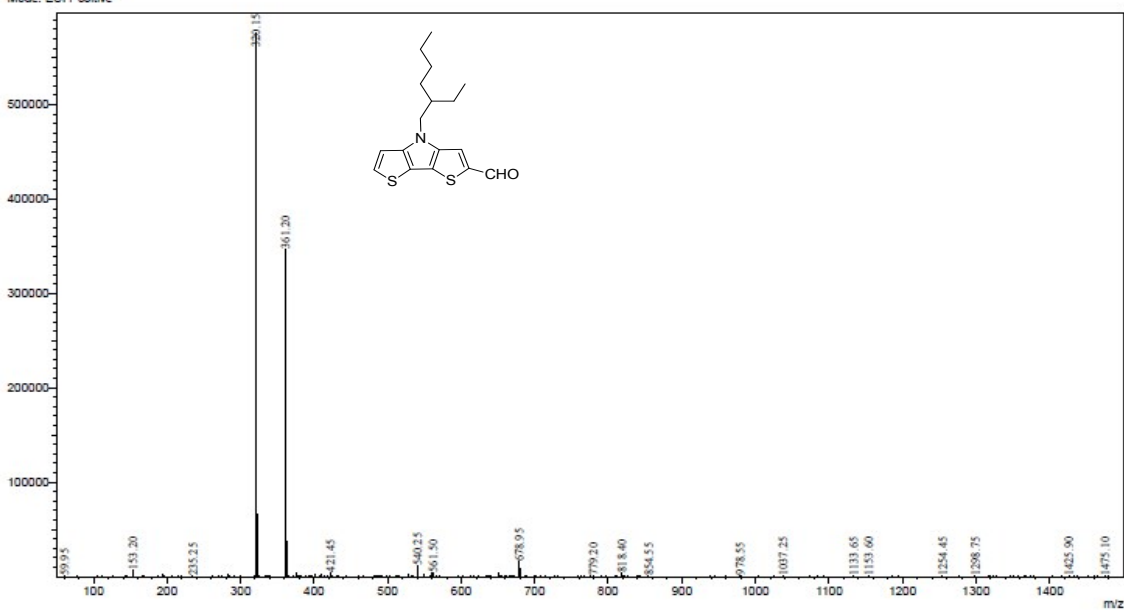


Fig. S20. ESI-MS spectrum of 4

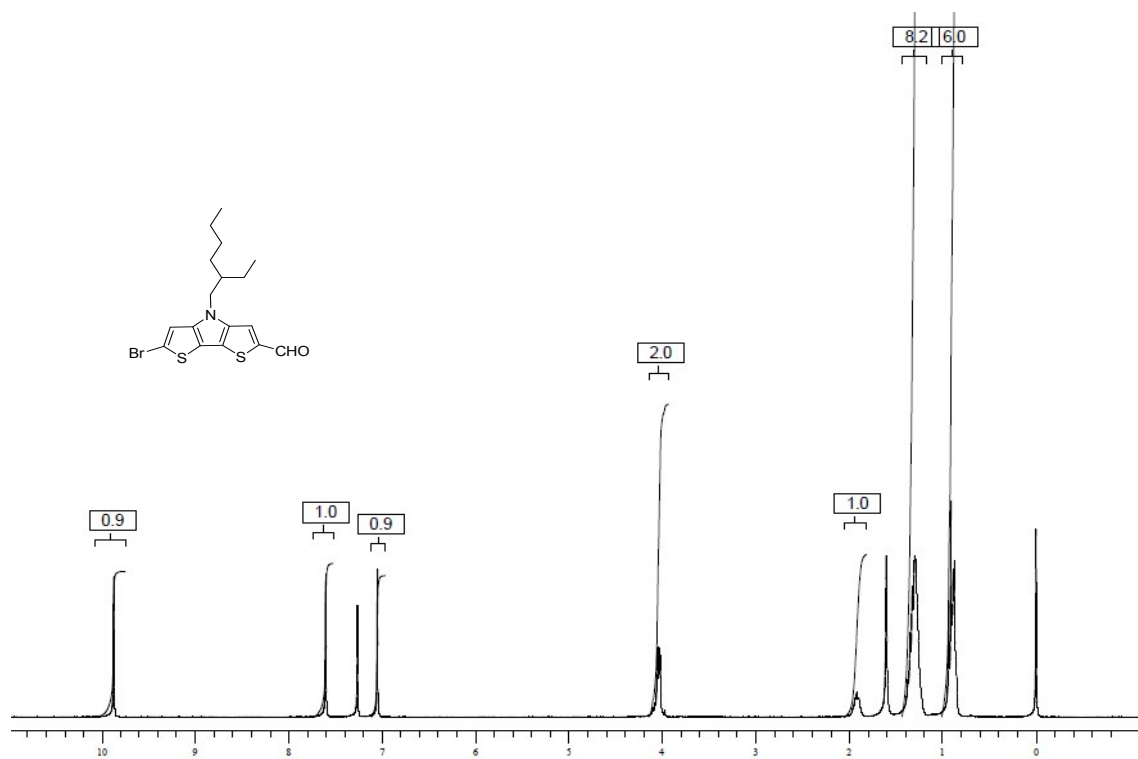


Fig. S21. ¹H NMR spectrum of **5**

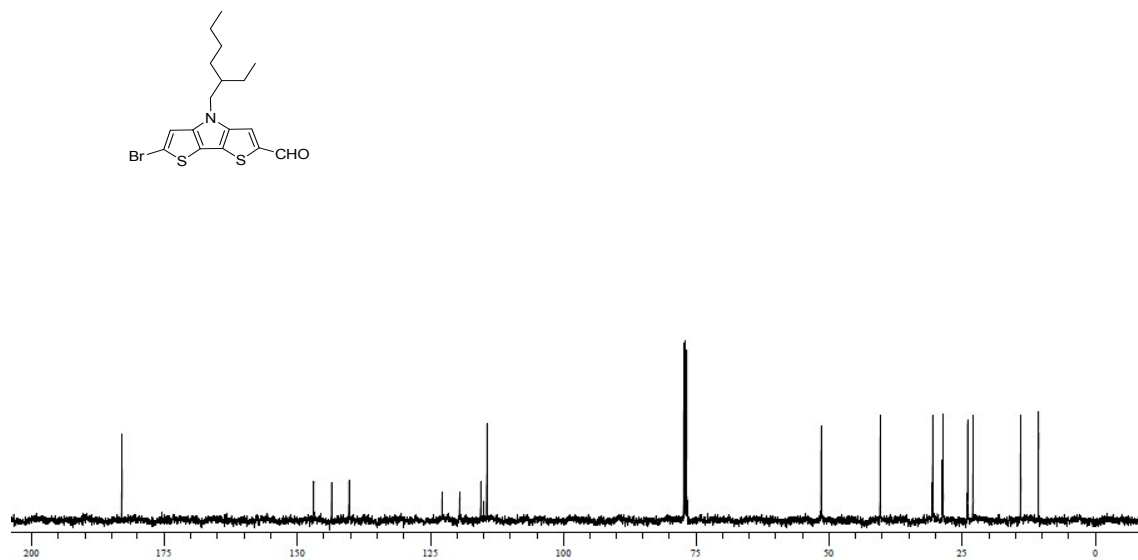


Fig. S22. ¹³C NMR spectrum of **5**

Sample Name : B Manohar reddy
 Sample ID : JRAO-MR-DTPBR
 Original Data File : D:\LCMS\Data\ESI-APCI Mass\2016\02-09-2016\JRAO-MR-DTPBR.lcd

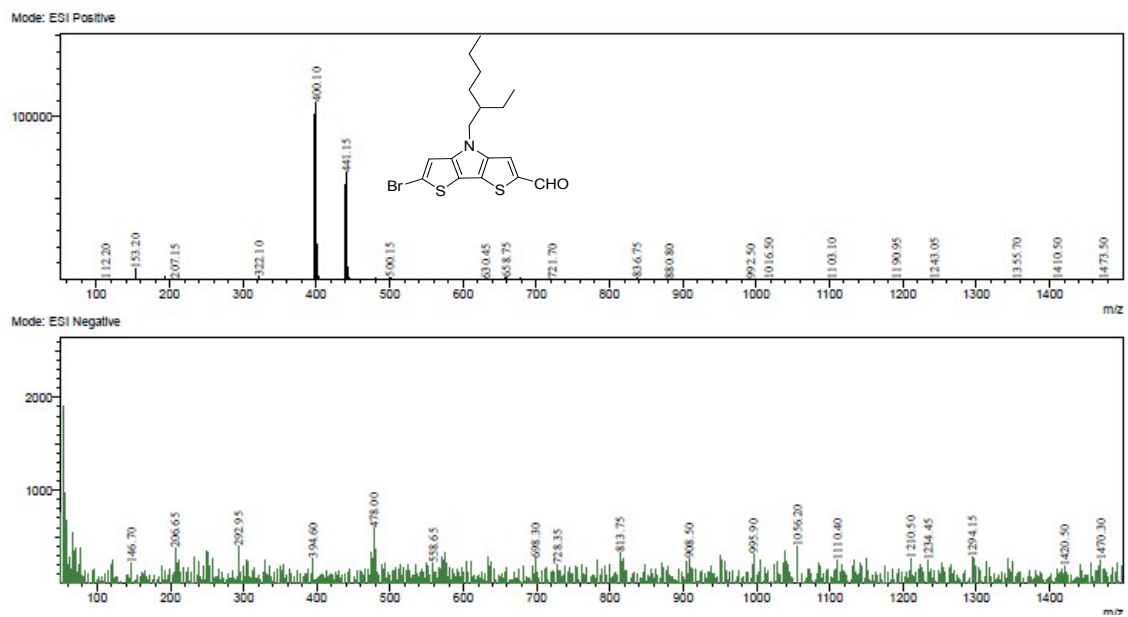


Fig. S23. ESI-MS spectrum of 5

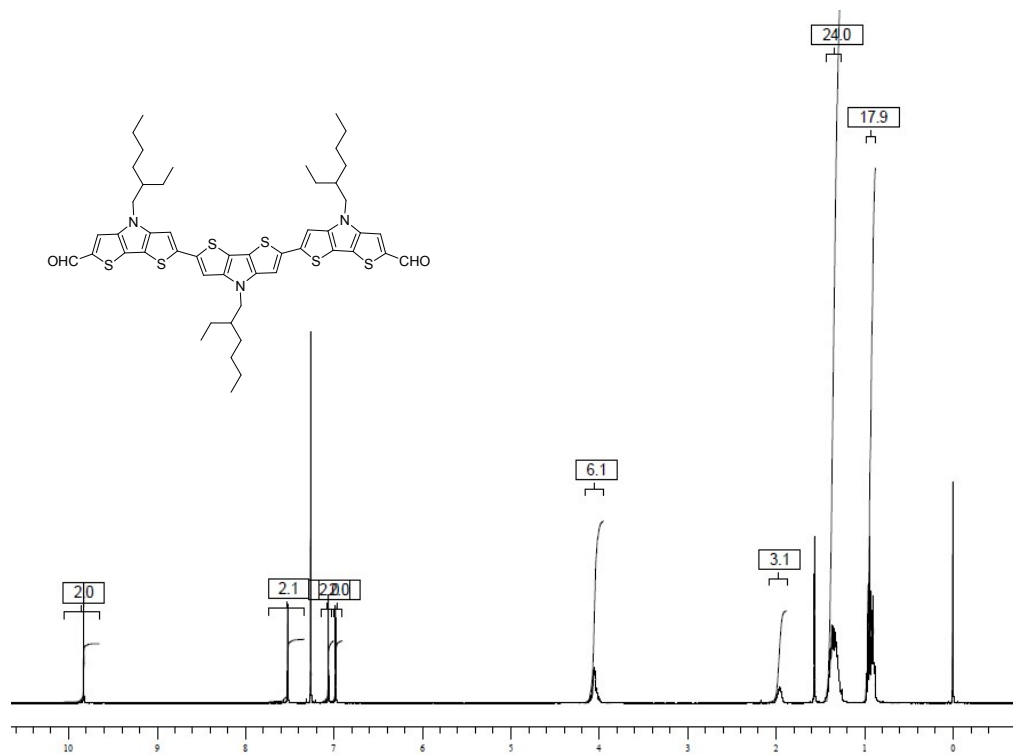


Fig. S24. ¹H NMR spectrum of 6

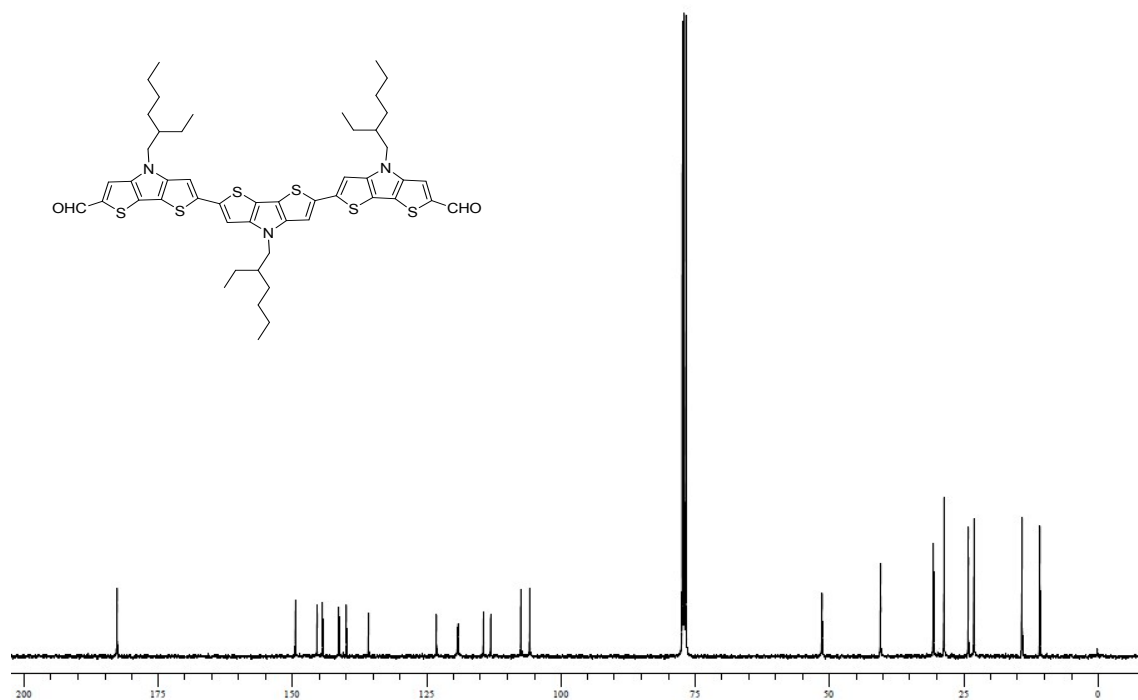


Fig. S25. ^{13}C NMR spectrum of **6**

MANOHAR REDDY , JRAO-MR-NA

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 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 65, Blanked, P.Ext. @ 1500 (bin 79)
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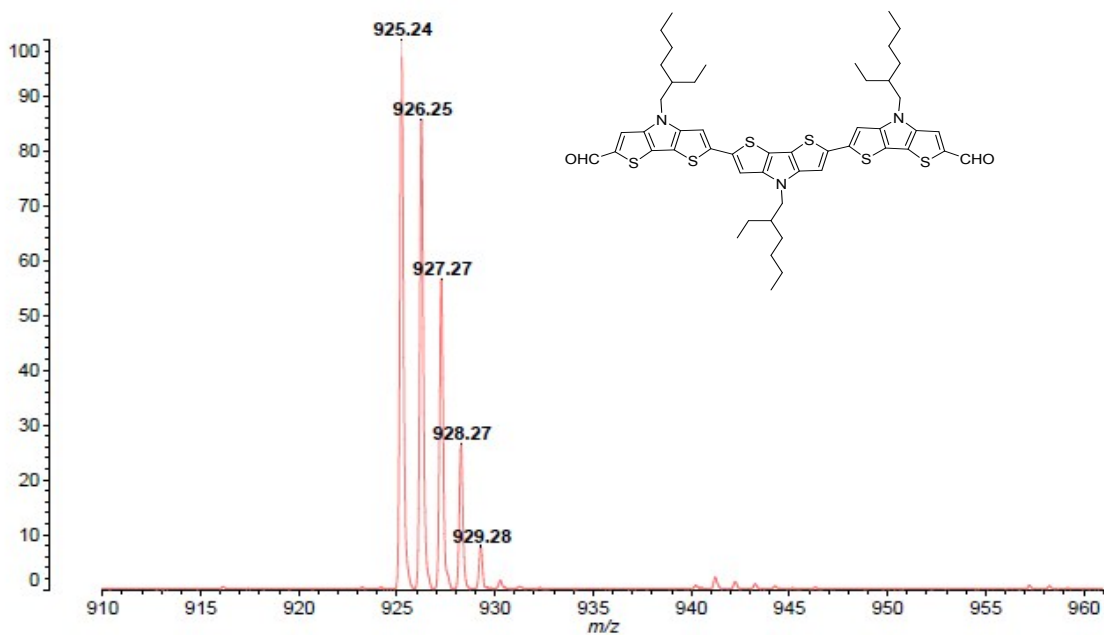


Fig. S26. ESI-MS spectrum of **6**

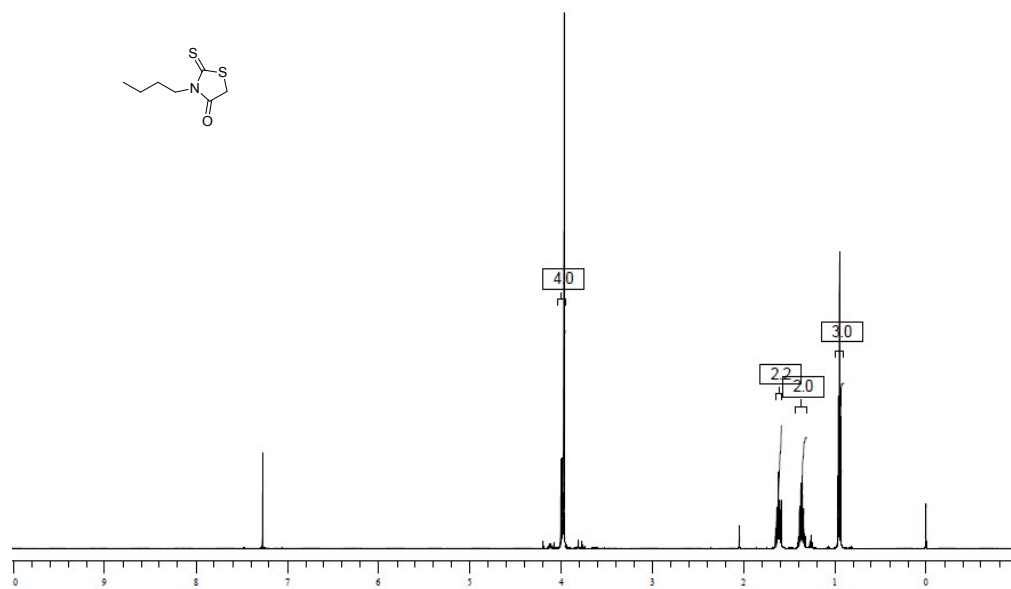


Fig. S27. ¹H NMR spectrum of *n*-butyl rhodanine