

Electronic Supplementary Information

Study on the effect of fluorine substitution on the photovoltaic properties of dithieno[3,2-*b*:2',3'-*d*]pyrrole-benzo[*c*][1,2,5]thiadiazole conjugate small molecule donor materials

Manohar Reddy Busireddy,^a Narendra Reddy Chereddy,^{a,*} Balaiah Shanigaram,^b Kotamarthi Bhanuprakash,^{b,*} Subhayan Biswas,^c Ganesh Datt Sharma^{c,*} Vaidya Jayathirtha Rao ^{a,d,*}

^a*Crop Protection Chemicals Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India.*

^b*Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India.*

^c*Department of Physics, The LNM Institute of Information Technology, Jamdoli, Jaipur, India.*

^d*AcSIR, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, India.*

Corresponding author Tel.: +91 40 27193933; Fax: +91 40 27193382

E-Mail: chereddynarendra@gmail.com (Narendra Reddy Chereddy); vaidya.opv@gmail.com (Vaidya Jayathirtha Rao); gdsharma273@gmail.com (Ganesh Datt Sharma); bhanu2505@yahoo.co.in (Kotamarthi Bhanuprakash)

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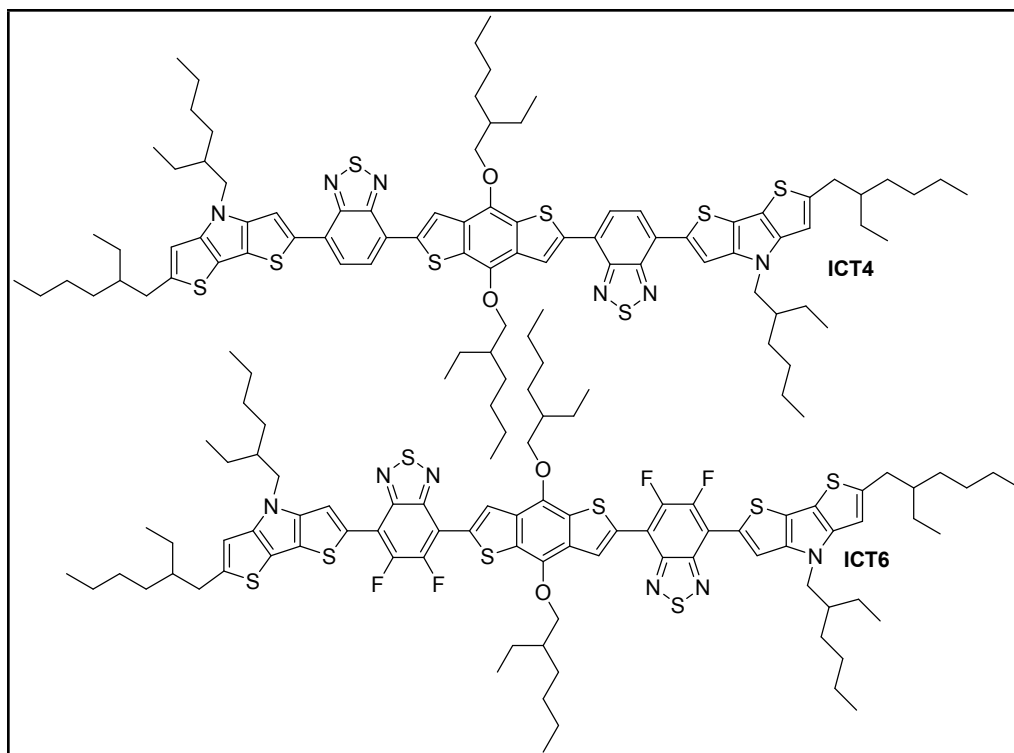


Fig. S1. Chemical structures of **ICT4** and **ICT6**

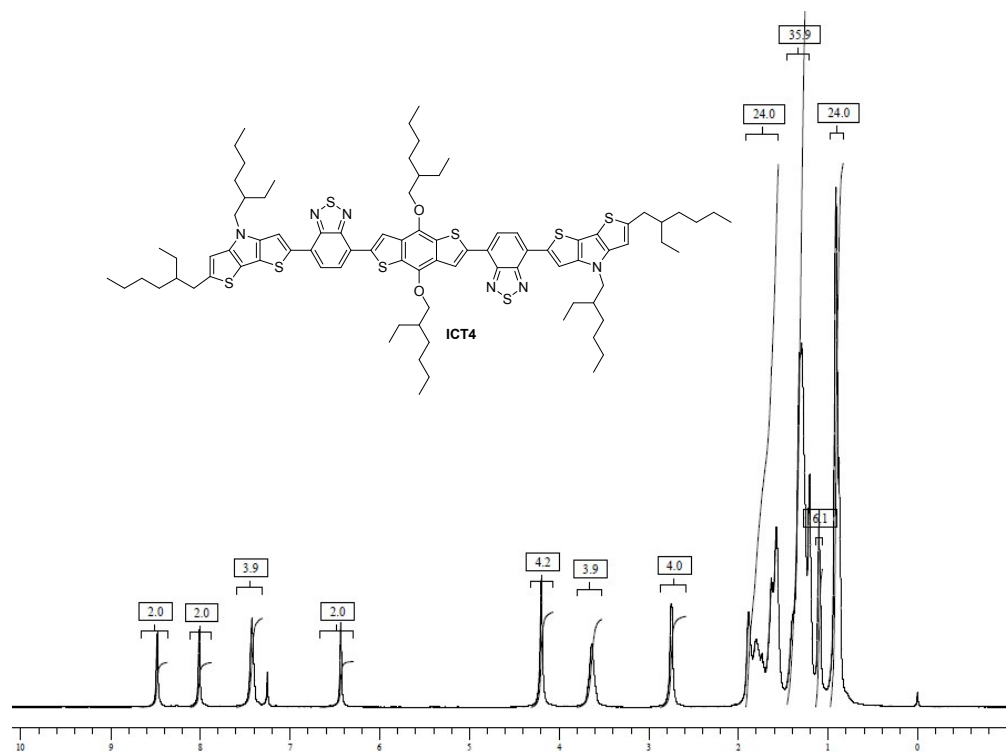


Fig. S2. ¹H NMR spectrum of **ICT4**

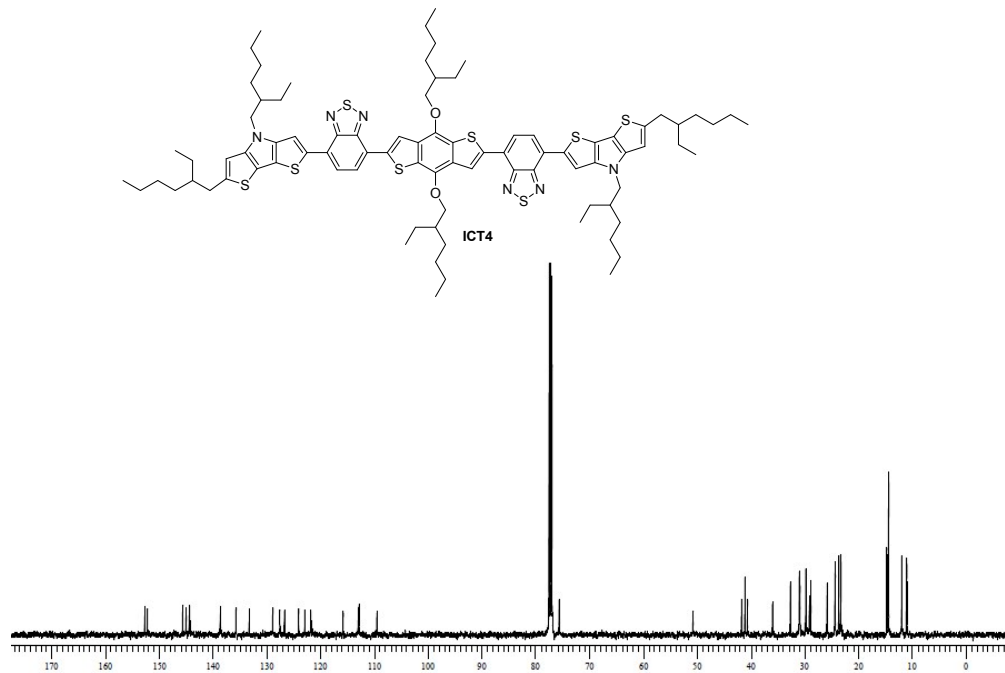


Fig. S3. ^{13}C NMR spectrum of ICT4

, MANOHAR REDDY, JRAO-MR-ICT4

Data: JRAO-MR-ICT40001.2C3[c] 23 Sep 2016 16:54 Cal: TOF MIX 23-09-16 RF 23 Sep 2016 16:33
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 72, Blanked, P.Ext. @ 2300 (bin 99)
 %Int. 52 mV[sum= 1146 mV] Profiles 1-22 Smooth Gauss 5

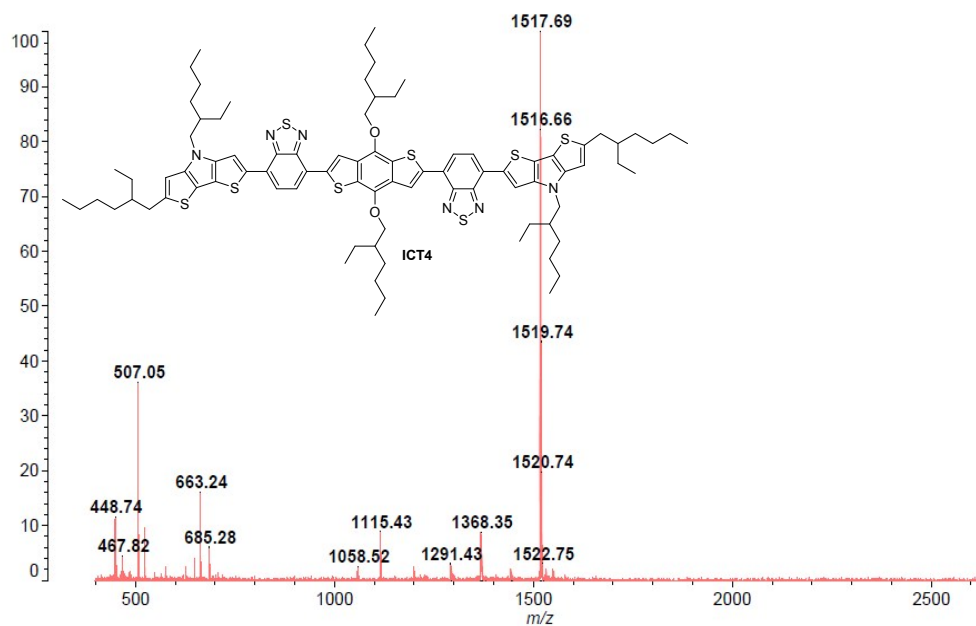
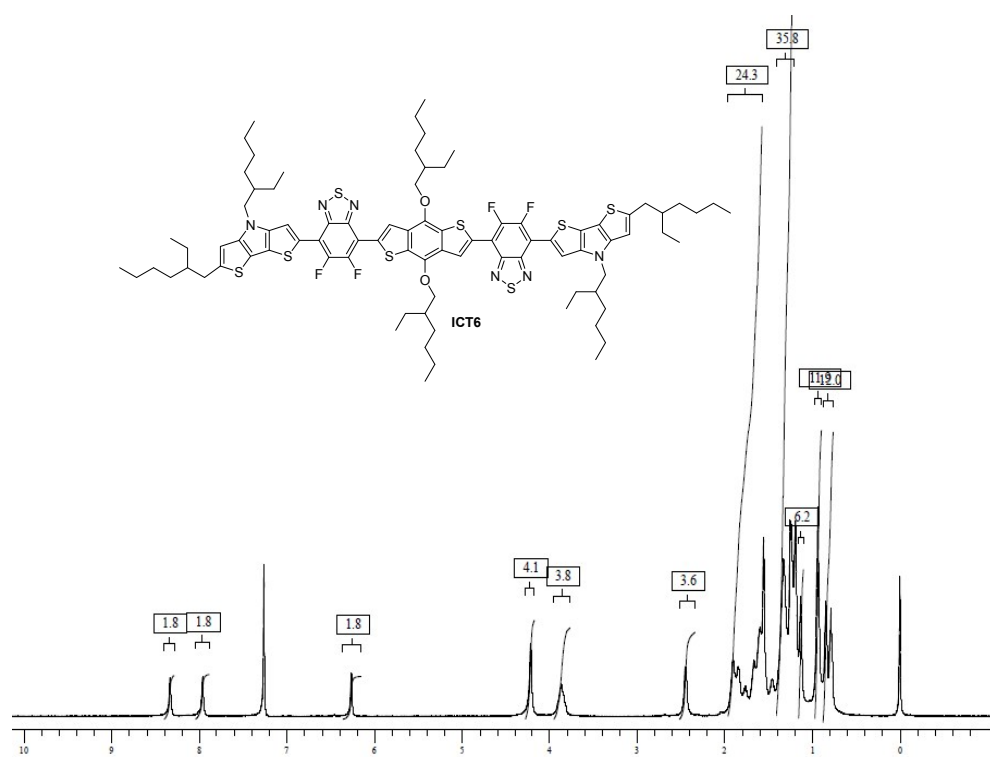


Fig. S4. MALDI-MS spectrum of ICT4



Data: JRAO-MR-ICT60001.2D1[c] 23 Sep 2016 16:56 Cal: TOF MIX 23-09-16 RF 23 Sep 2016 16:33
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 75, Blanked, P.Ext. @ 2300 (bin 99)
 %Int. 199 mV[sum= 4383 mV] Profiles 1-22 Smooth Gauss 5

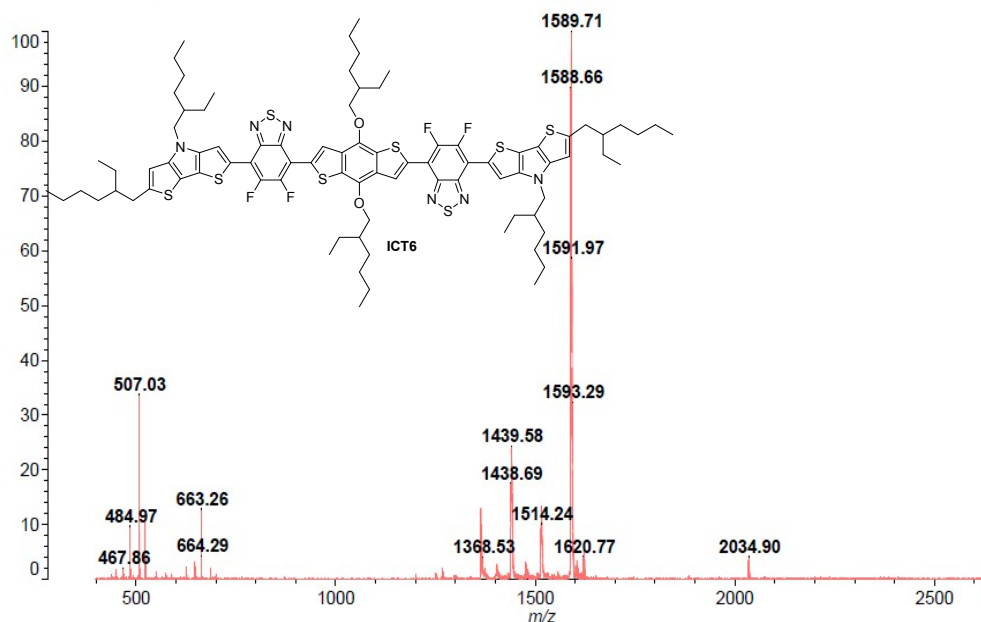


Fig. S7. MALDI-MS spectrum of ICT6

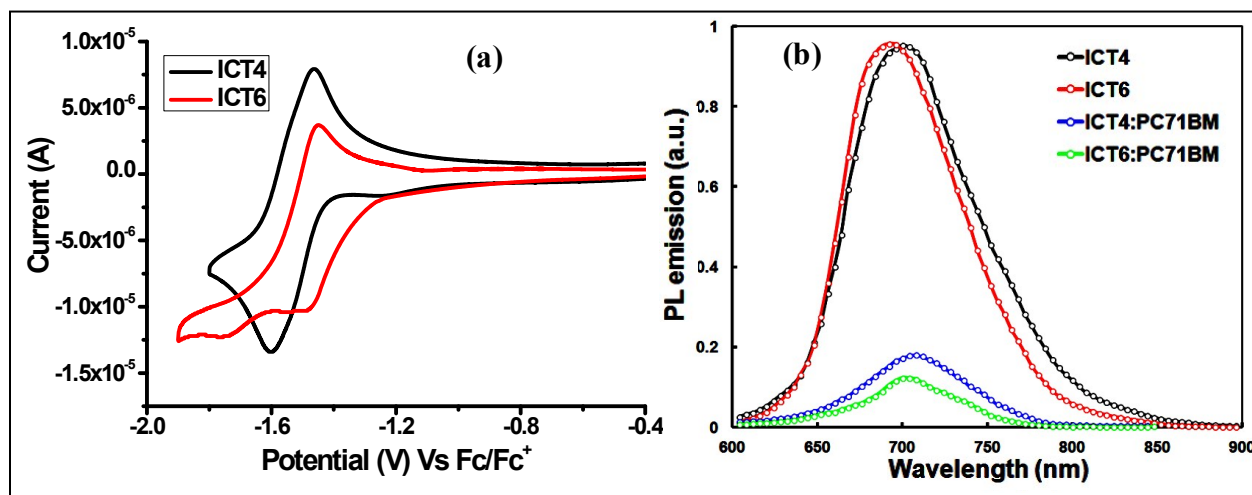


Fig. S8. Cyclic voltammograms (a) of ICT4 and ICT6 and PL emission spectra (b) of ICT4, ICT6, ICT4:PC₇₁BM and ICT6:PC₇₁BM thin films

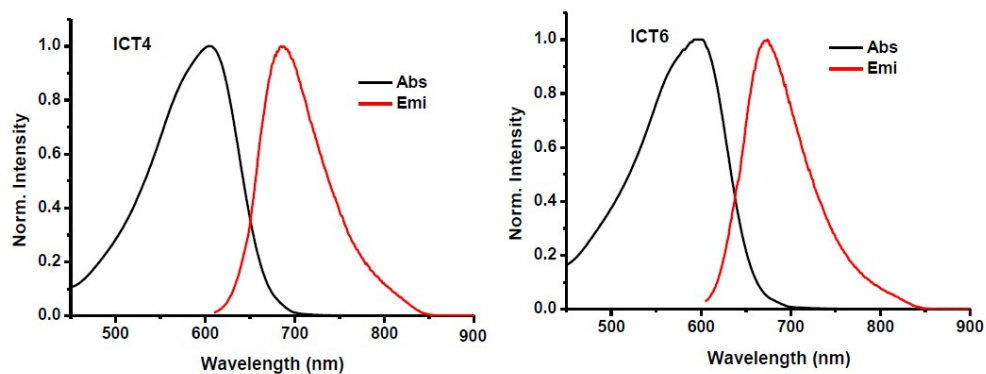


Fig. S9 UV-Vis absorption and emission spectra of **ICT4** and **ICT6** (10 μ M) in chloroform

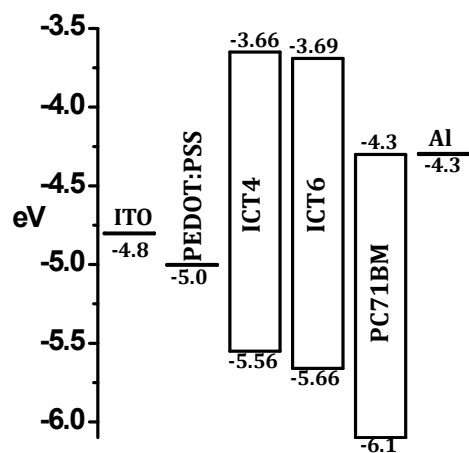


Fig. S10 HOMO and LUMO energy levels of **ICT4**, **ICT6** and PC₇₁BM materials

Material	ICT4	ICT6
E_{tran} (kcal/mol)	 0.0	 0.0
E_{NH} (kcal/mol)	 3.35	 0.57
E_{cis} (kcal/mol)	 6.33	 1.68

Fig. S11 Relative energies of cis and trans and NH conformations of **ICT4** and **ICT6** obtained at B3LYP/6-31G(d,p) level of theory.

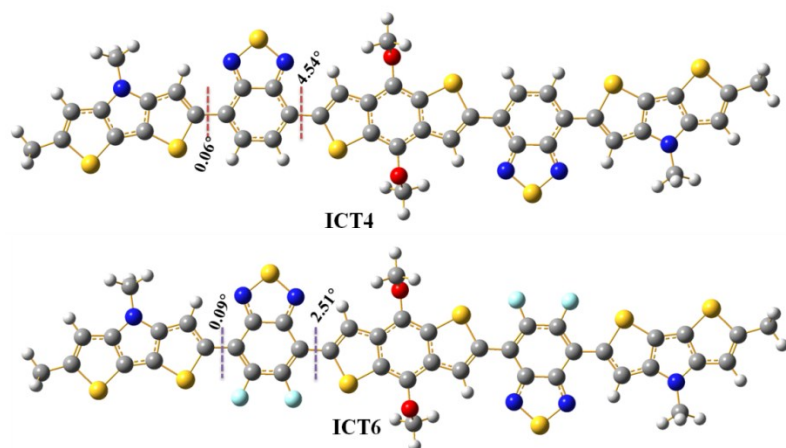


Fig. S12 Pictorial representation of dihedral angles in optimized geometries of **ICT4** and **ICT6** at B3LYP/6-31G(d,p) level of theory.

Table S1 Calculated properties of **ICT4** and **ICT6** at M06-2X/6-311G(d,p) level in chloroform solvent. HOMO and LUMO energies (eV), HOMO–LUMO gap, HLG (eV), Optical gap, OG (eV), oscillator strength, f , the wavelengths of the first excitation and excitations with the largest oscillator strengths, the main contributions to the first excited state, (CI) and the dipole moment, μ_g (D).

Molecule	HOMO ^a (eV)	LUMO (eV)	HLG (eV)	λ (nm)	OG (eV)	f	CI ^a	μ_g ^b (D)
ICT4	-6.08	-2.43	3.65	569	2.178	2.883	H-1→L+1 (19%), HOMO→LUMO (76%)	0.0
ICT6	-6.19	-2.53	3.66	559	2.217	2.996	H-1→L+1 (19%), HOMO→LUMO (76%)	0.0

^a HOMO and LUMO values are obtained from M06-2X/6-311G(d,p) in chloroform.

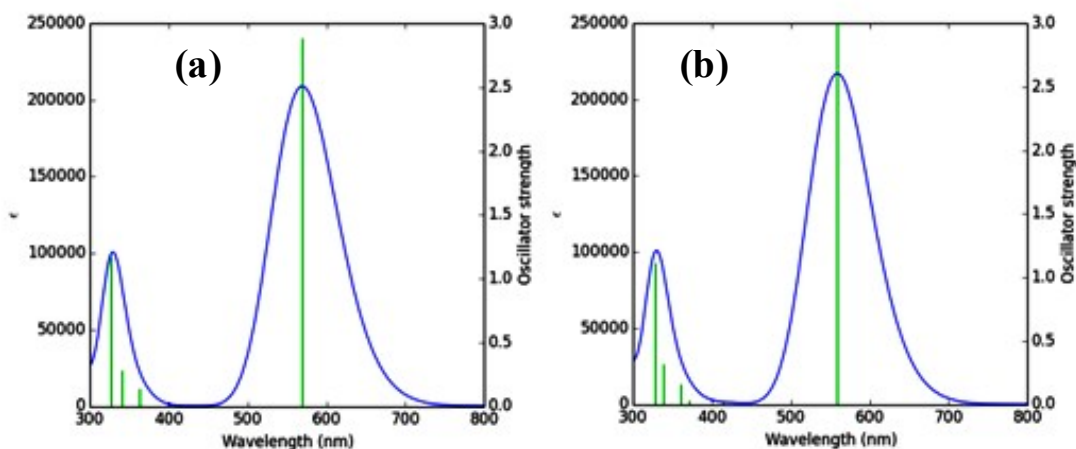
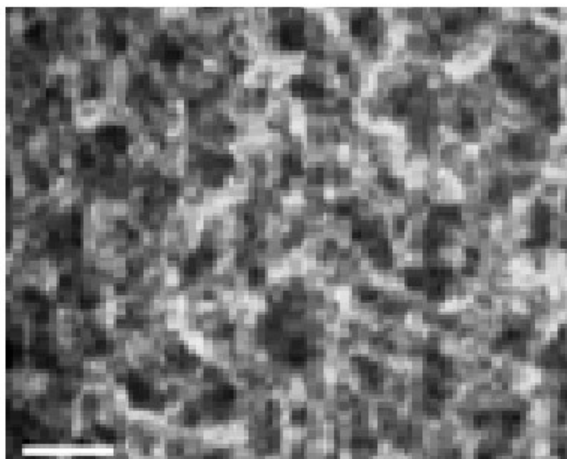
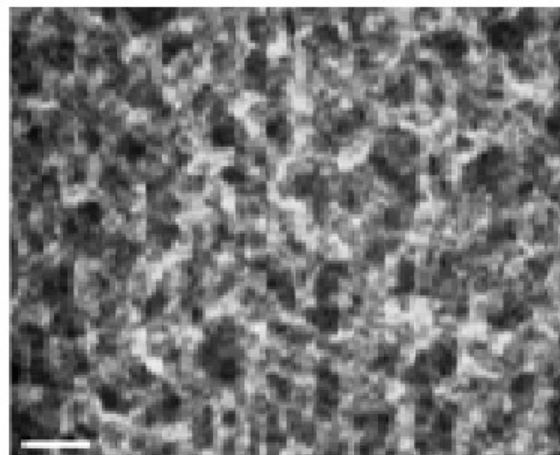


Fig. S13 M06-2X/6-311G(d,p) simulated absorption spectra of **ICT4** (a) and **ICT6** (b) in chloroform solvent.



ICT4:PC71BM



ICT6:PC71BM

Fig. S14. Transmission electron microscopy (TEM) images of as cast **ICT4:PC₇₁BM** and **ICT6:PC₇₁BM** thin films, bar is 100 nm

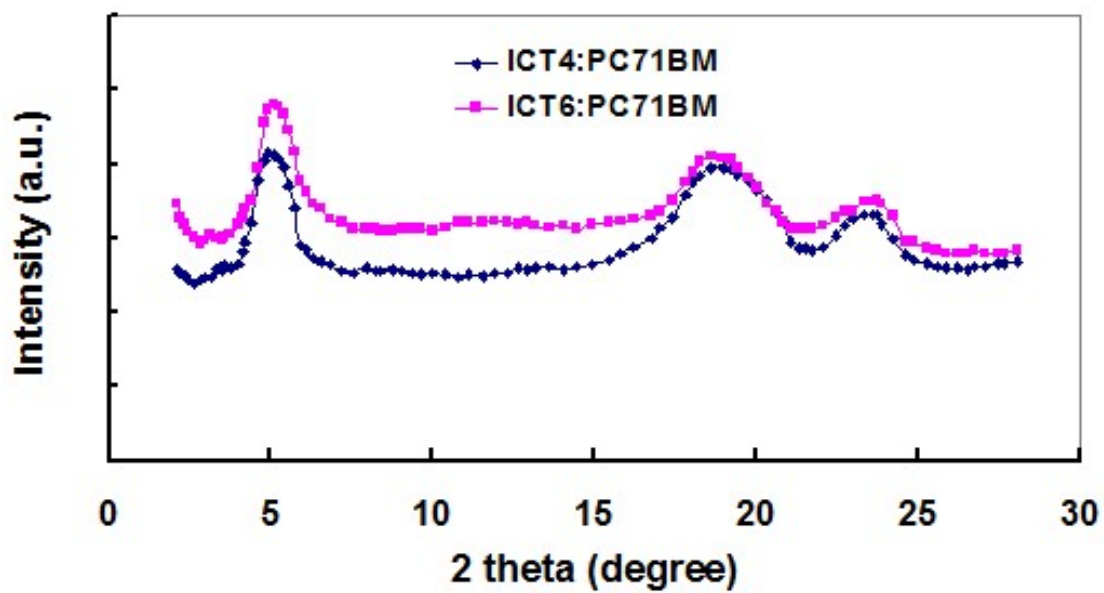


Fig. S15. X-ray diffraction of as cast **ICT4:PC₇₁BM** and **ICT6:PC₇₁BM** blend thin films

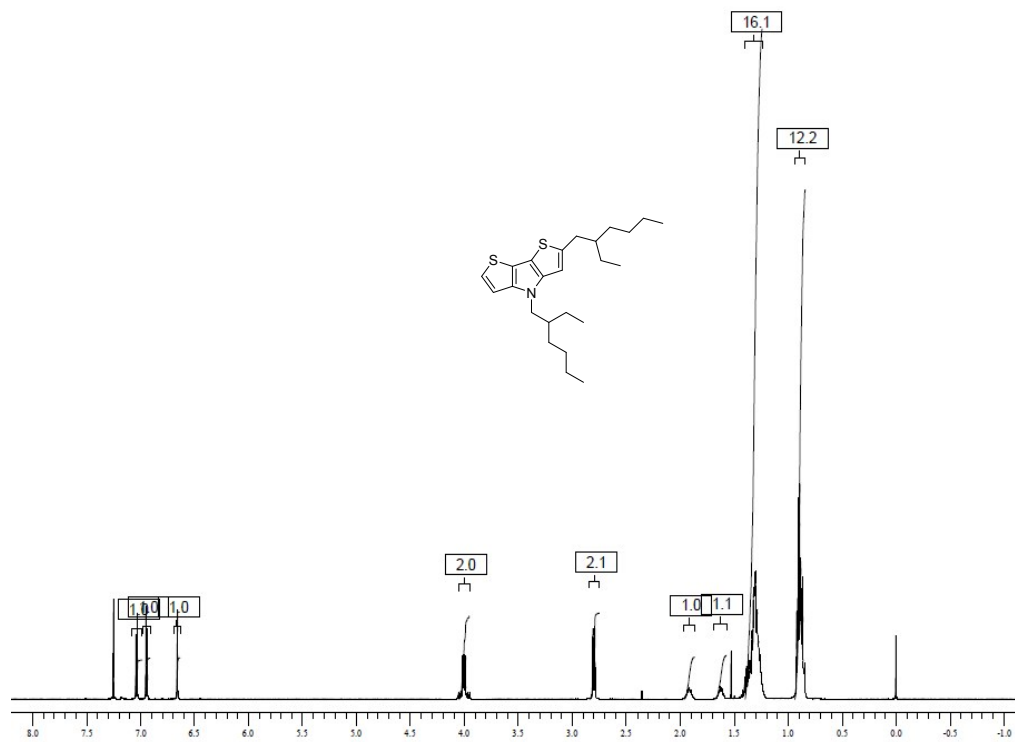


Fig. S16. ¹H NMR spectrum of **7**

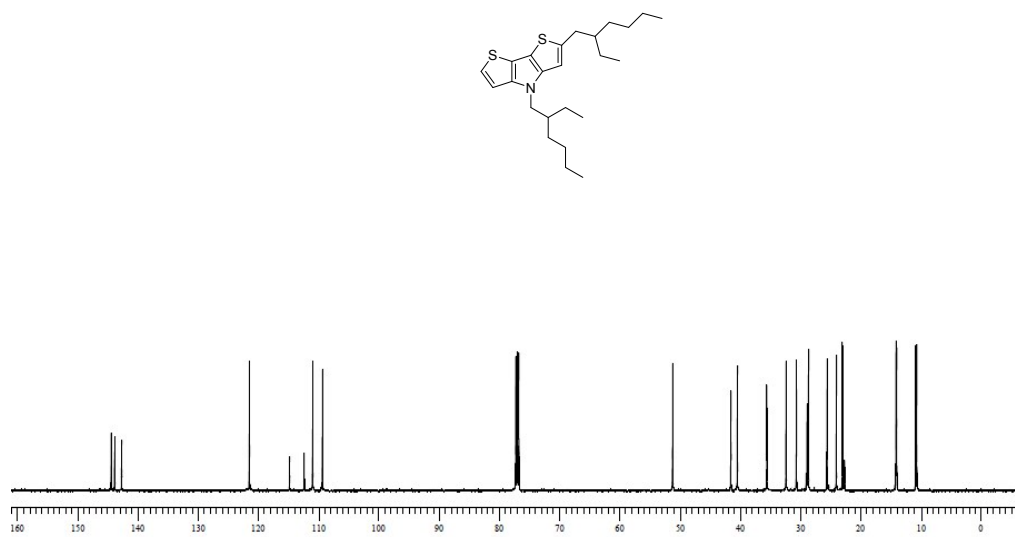


Fig. S17. ¹³C NMR spectrum of **7**

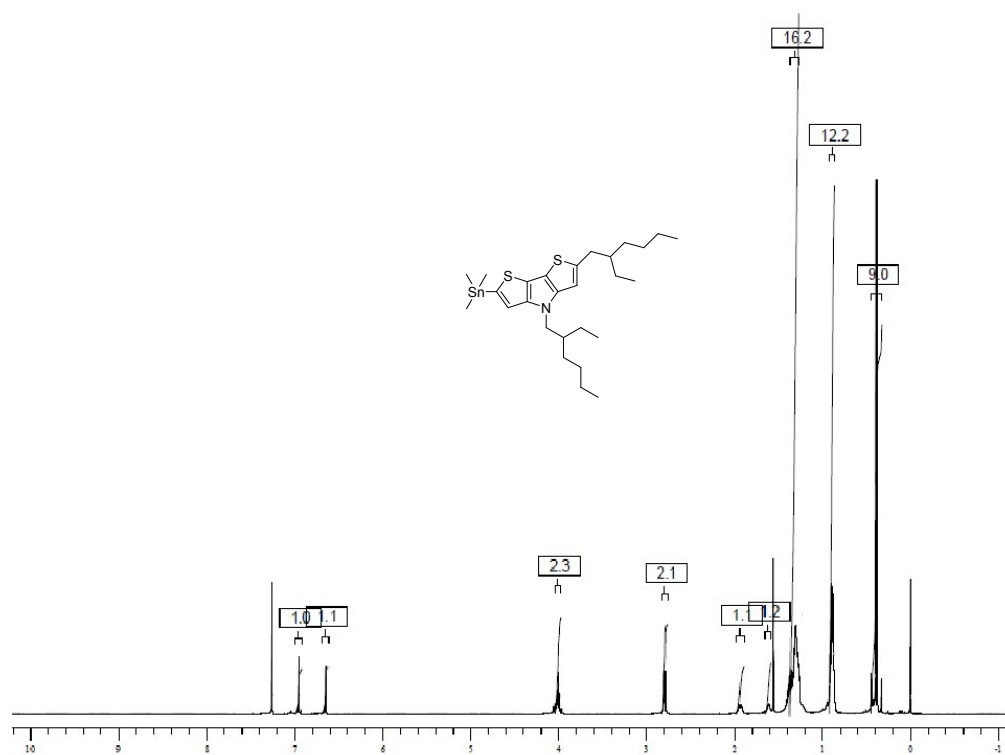


Fig. S18. ^1H NMR spectrum of **8**

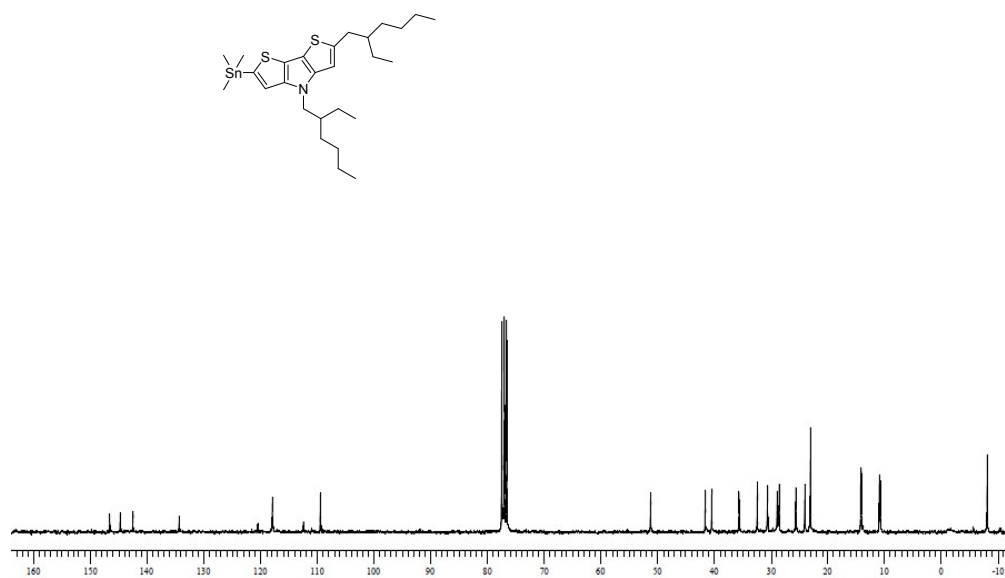


Fig. S19. ^{13}C NMR spectrum of **8**

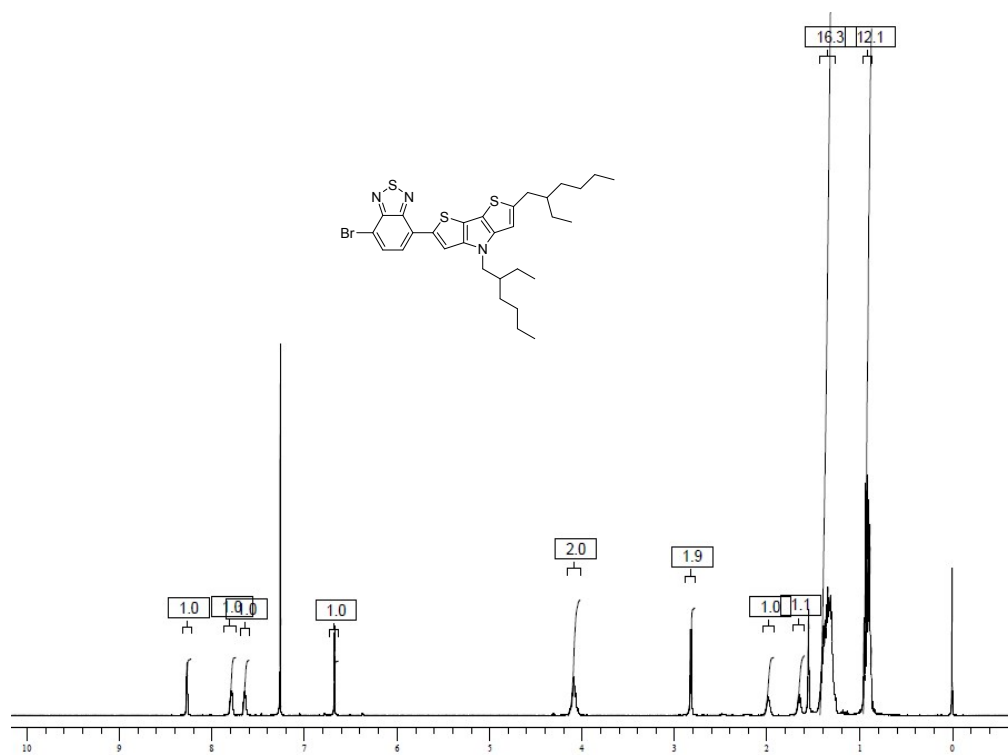


Fig. S20. ^1H NMR spectrum of **9**

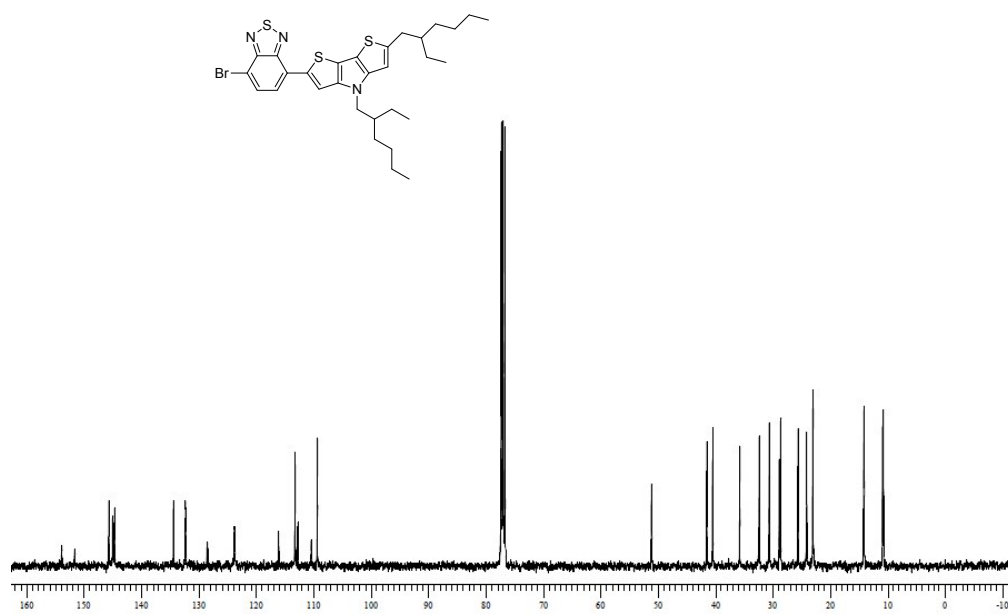


Fig. S21. ^{13}C NMR spectrum of **9**

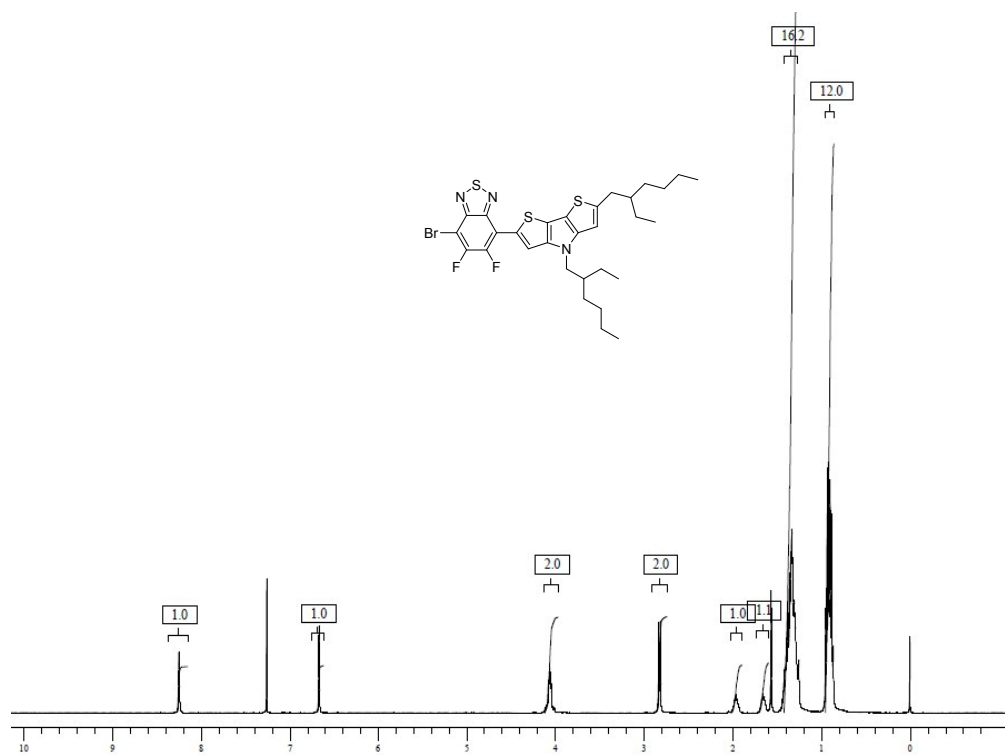


Fig. S22. ¹H NMR spectrum of **10**

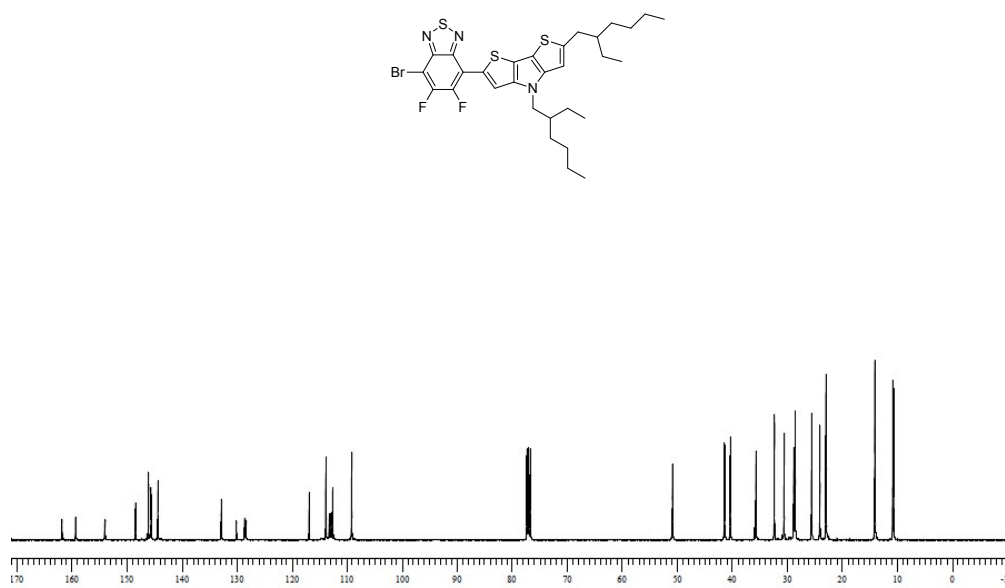


Fig. S23. ¹³C NMR spectrum of **10**