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

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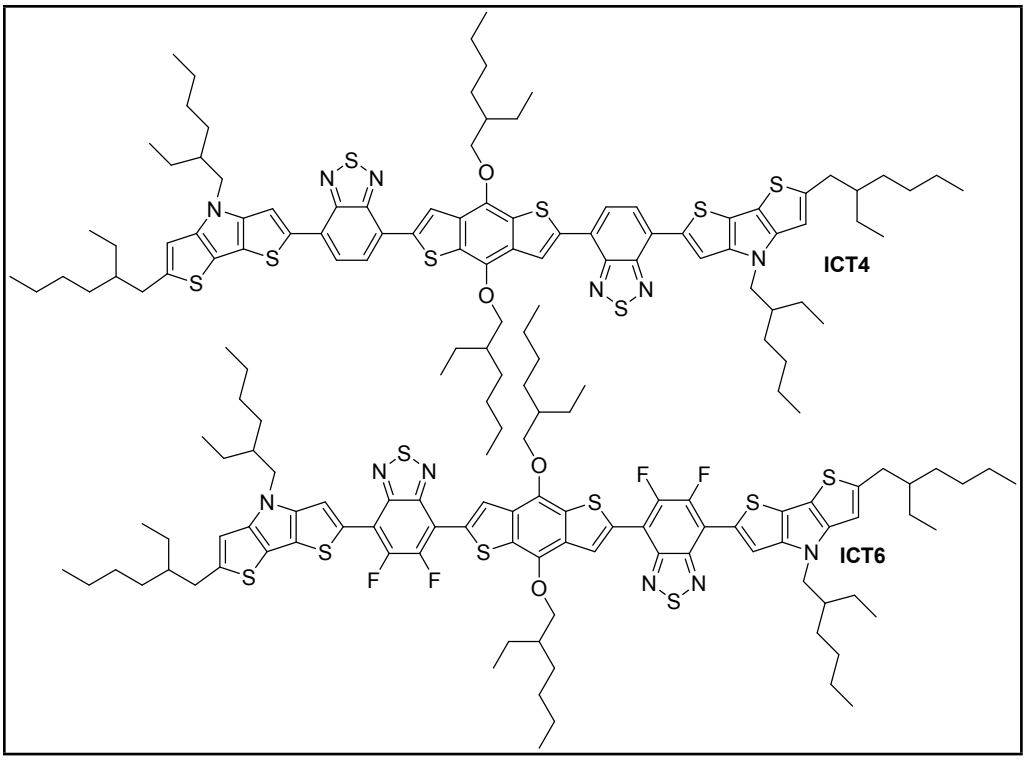


Fig. S1. Chemical structures of **ICT4** and **ICT6**

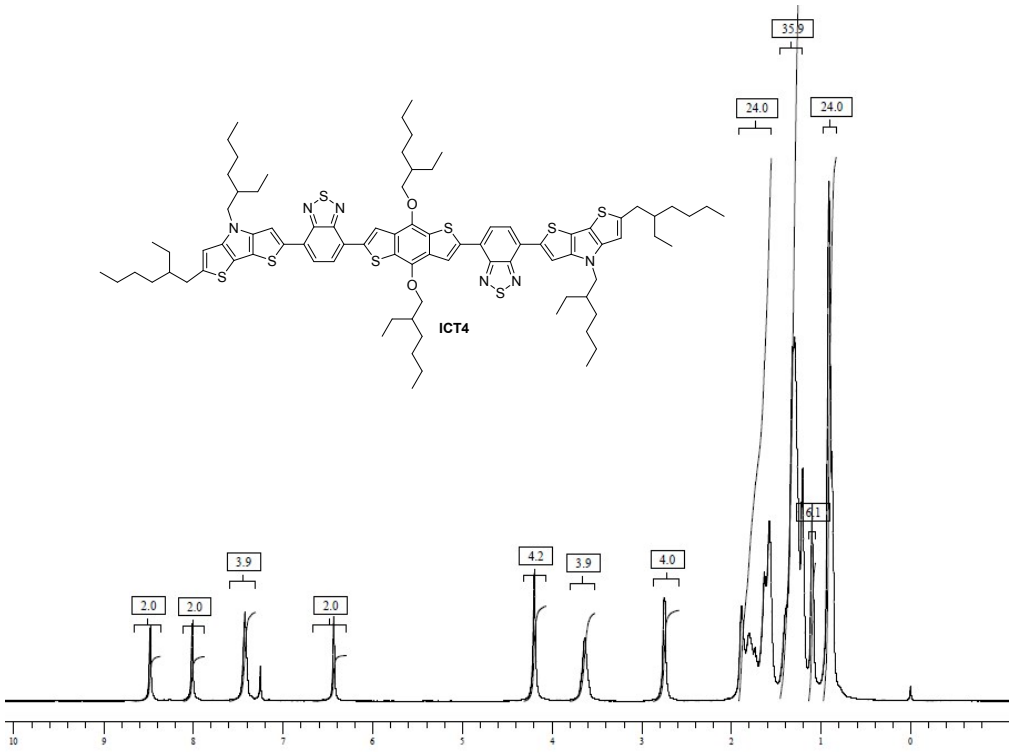


Fig. S2. ^{1}H NMR spectrum of **ICT4**

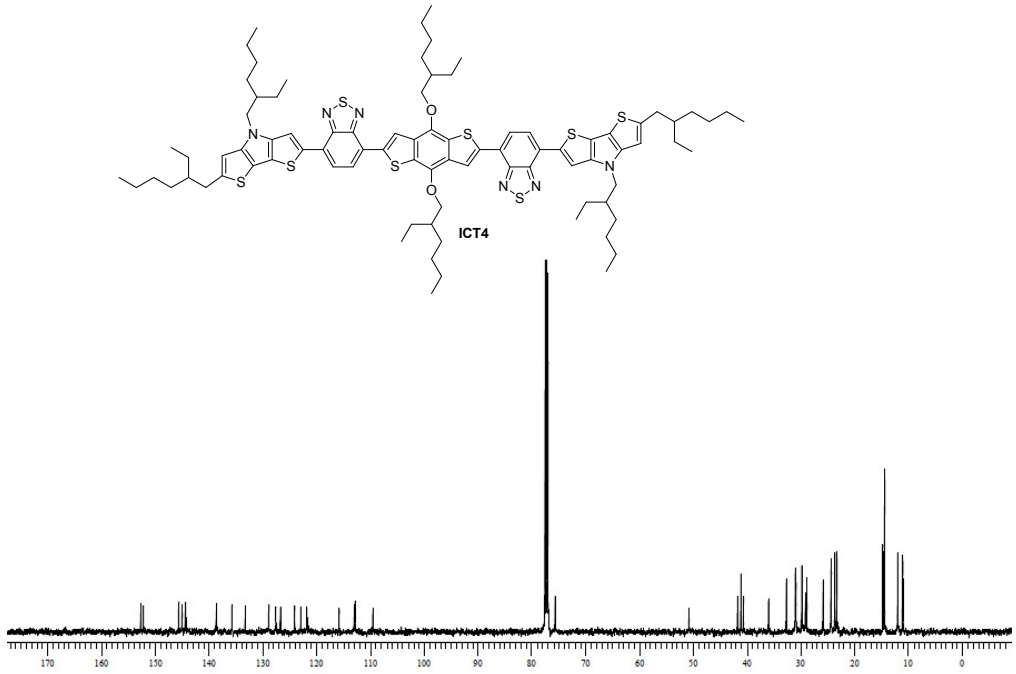


Fig. S3. ^{13}C NMR spectrum of **ICT4**

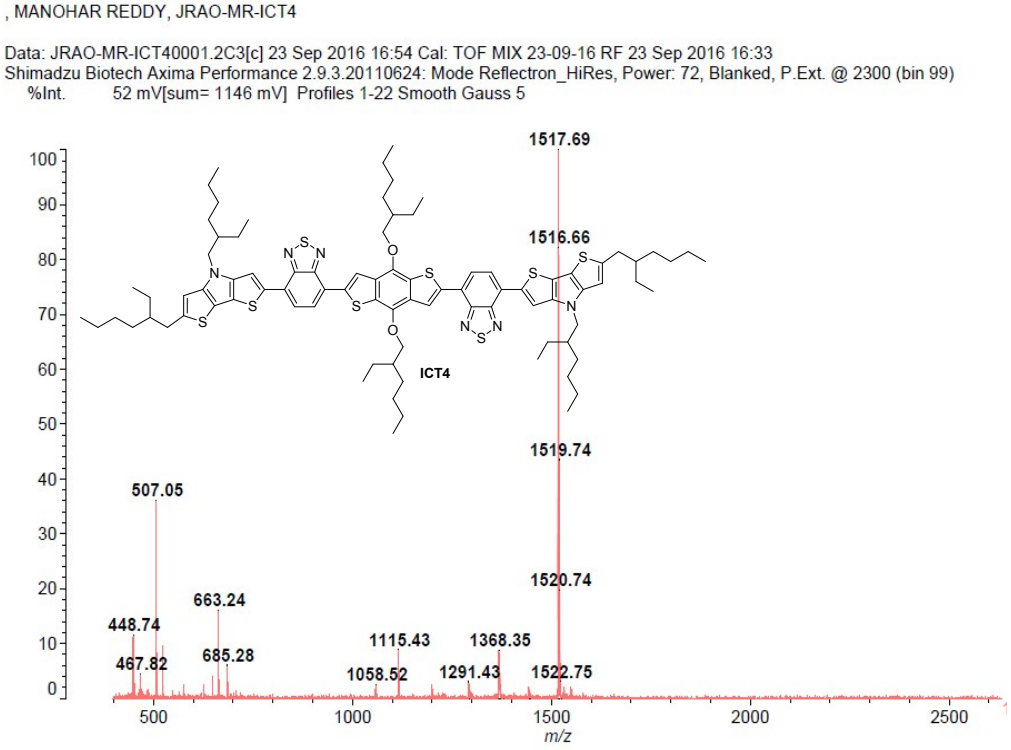


Fig. S4. MALDI-MS spectrum of **ICT4**

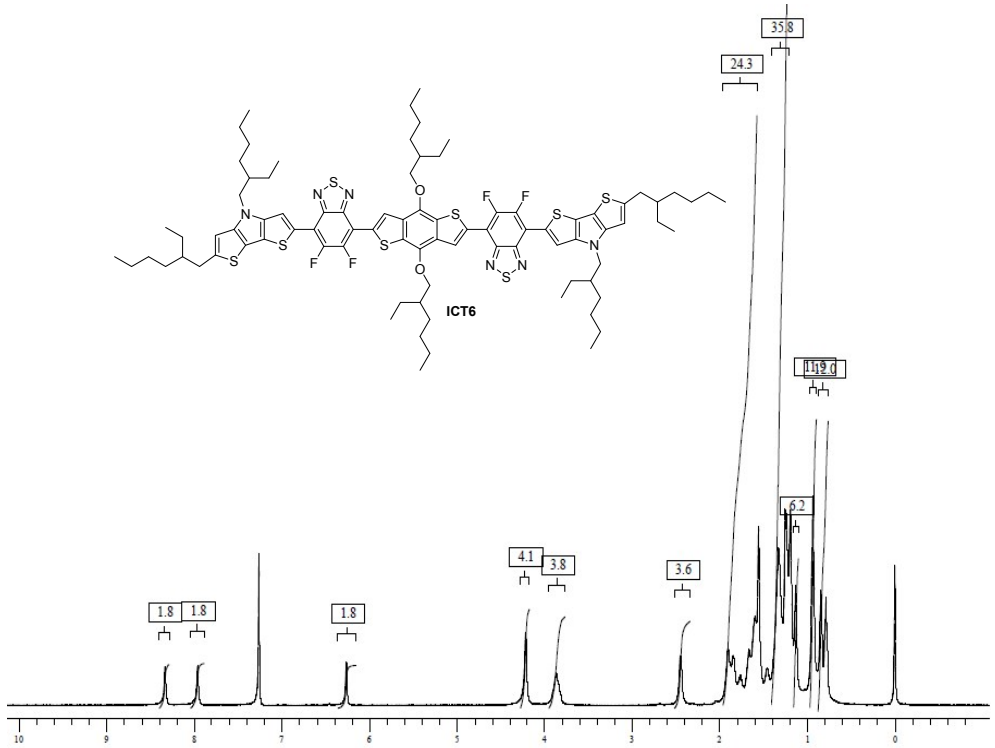


Fig. S5. ^{1}H NMR spectrum of **ICT6**

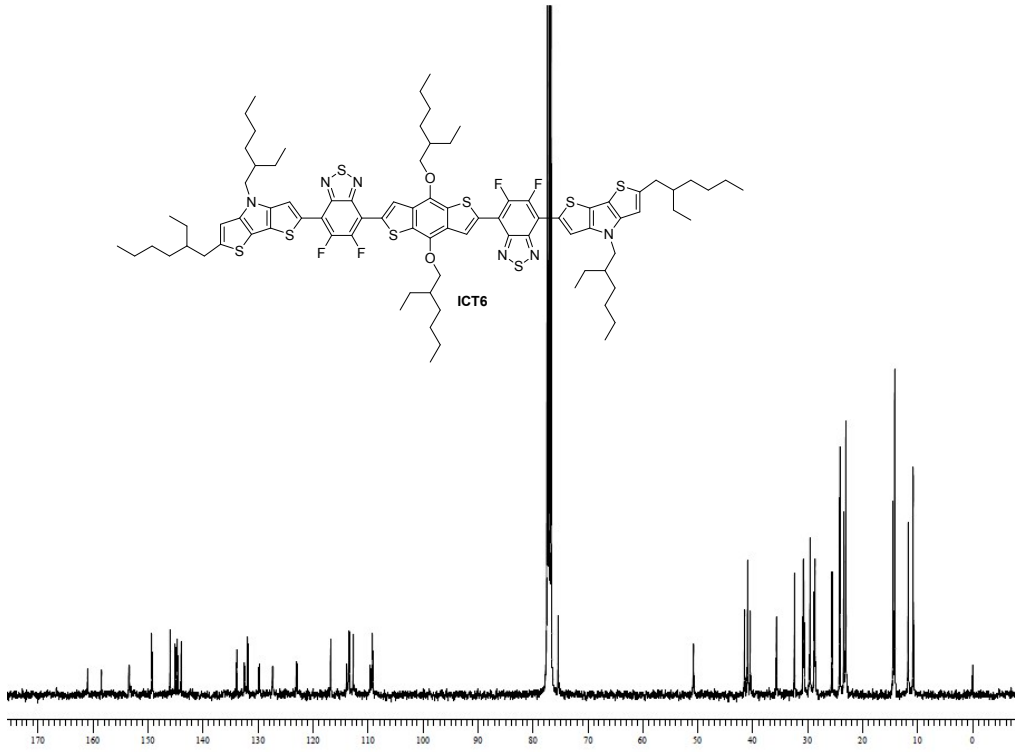


Fig. S6. ^{13}C NMR spectrum of **ICT6**

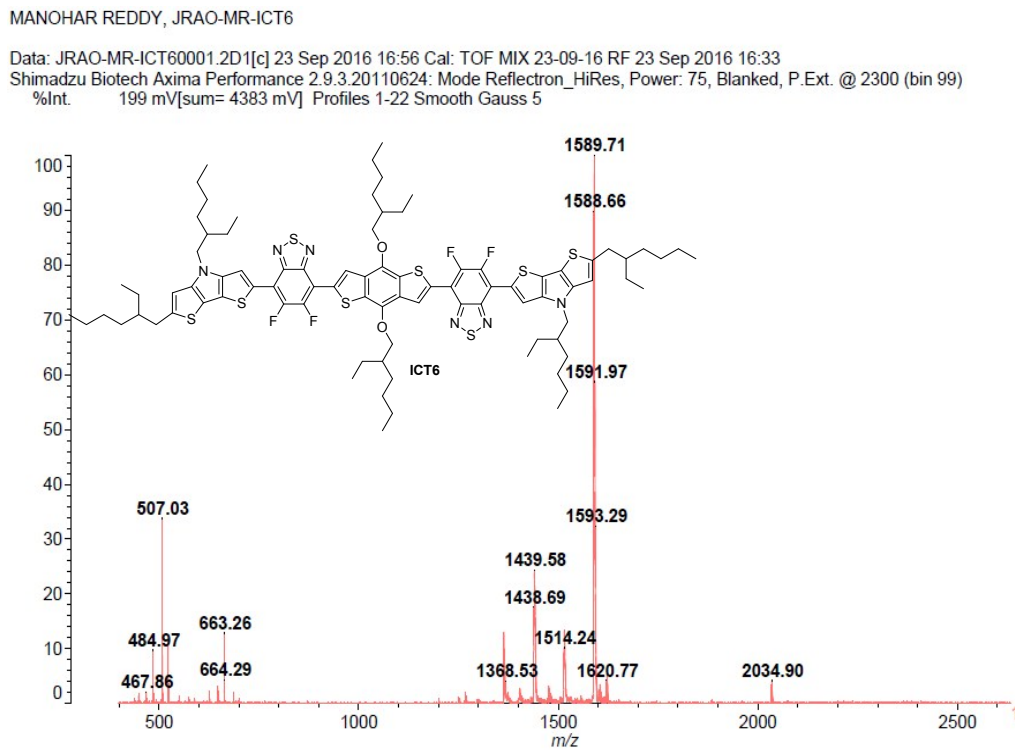


Fig. S7. MALDI-MS spectrum of **ICT6**

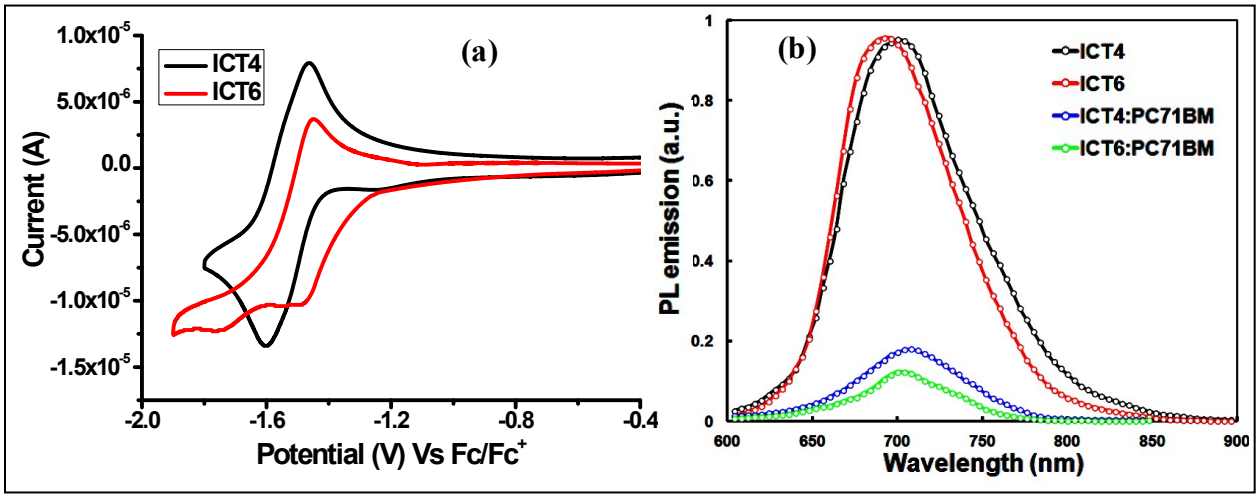


Fig. S8. Cylcic voltammograms (**a**) of **ICT4** and **ICT6** and PL emission spectra (**b**) of **ICT4**, **ICT6**, **ICT4**:$PC_{71}BM$ and **ICT6**:$PC_{71}BM$ thin films

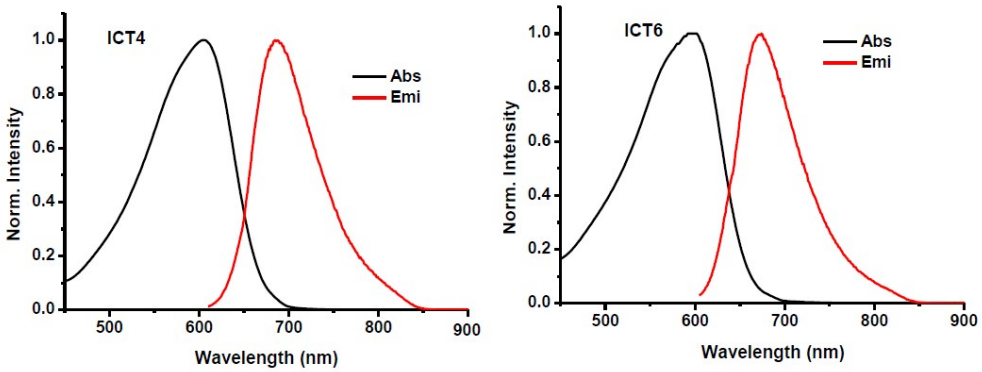


Fig. S9 UV-Vis absorption and emission spectra of **ICT4** and **ICT6** (10μM) in chloroform

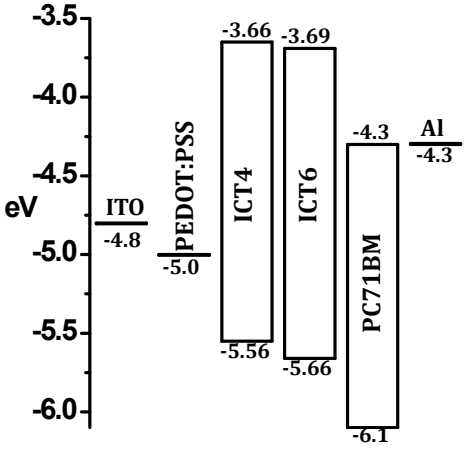


Fig. S10 HOMO and LUMO energy levels of **ICT4**, **ICT6** and $PC_{71}BM$ materials

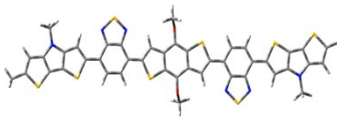
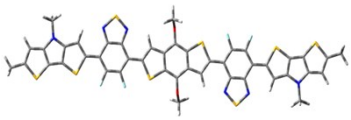
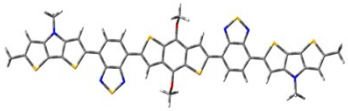
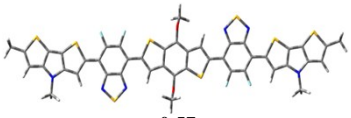
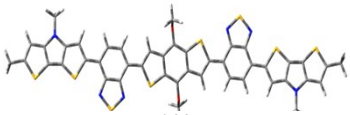
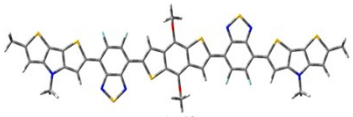
Material	ICT4	ICT6
E_{tran} (kcal/mol)	 0.0	 0.0
E_{NH} (kcal/mol)	 3.35	 0.57
E_{cis} (kcal/mol)	 6.33	 1.68

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.

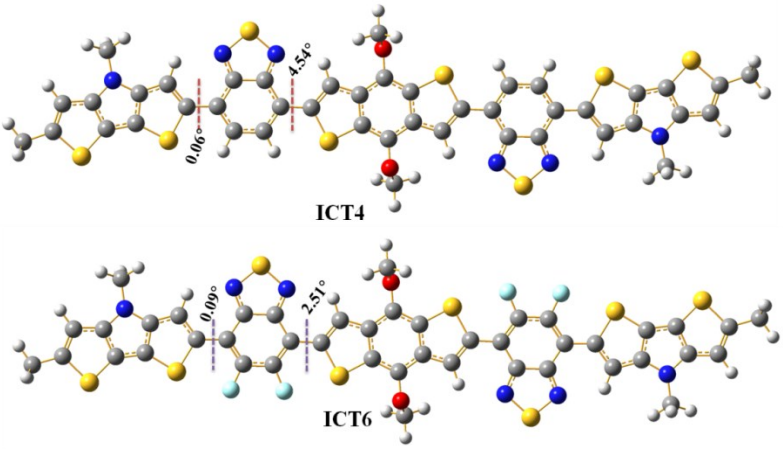


Fig. S12 Pictorial representation of dihedral angles in optimized geometries of **ICT4** and **ICT6** at B3LYP/6-31G(d,p) level of theory.

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.

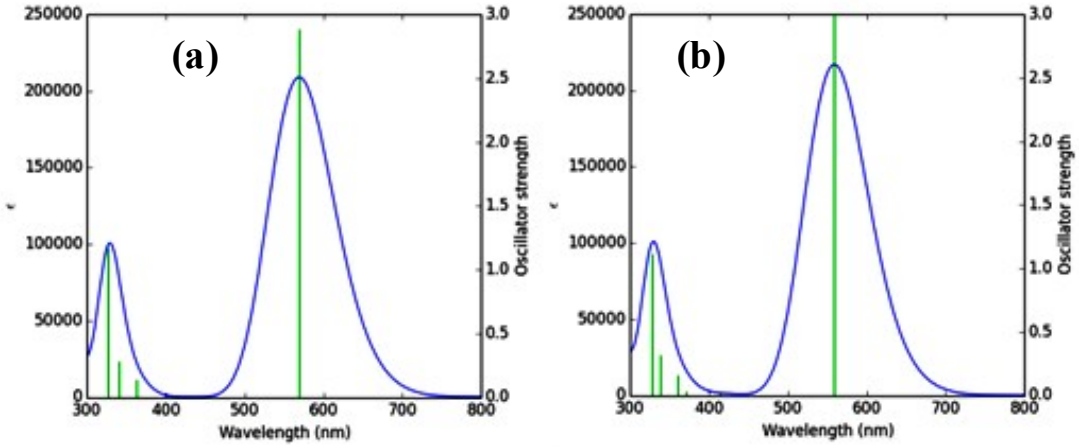


Fig. S13 M06-2X/6-311G(d,p) simulated absorption spectra of **ICT4** (**a**) and **ICT6** (**b**) in chloroform solvent.

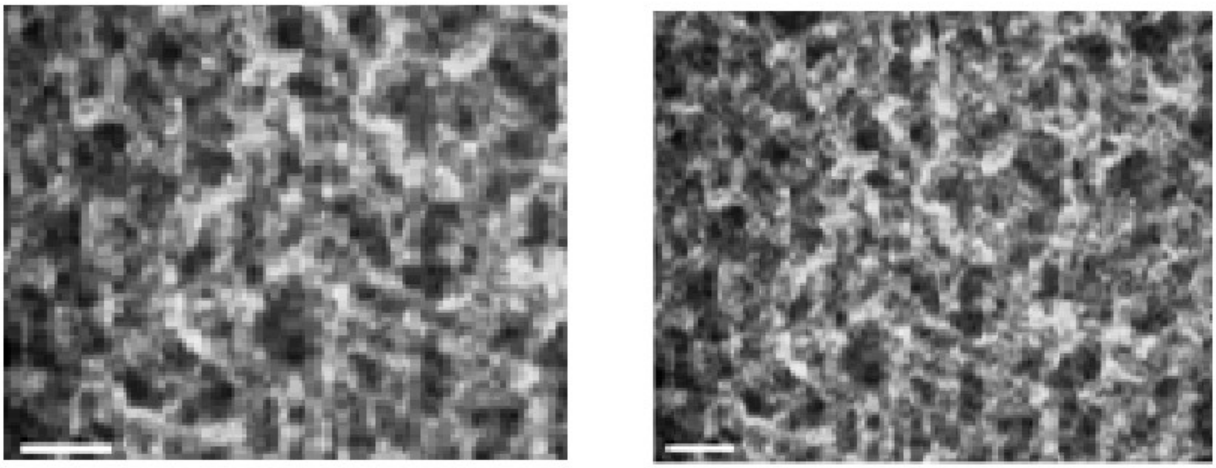


Fig. S14. Transmission electron microscopy (TEM) images of as cast **ICT4**:$PC_{71}BM$ and **ICT6**:$PC_{71}BM$ thin films, bar is 100 nm

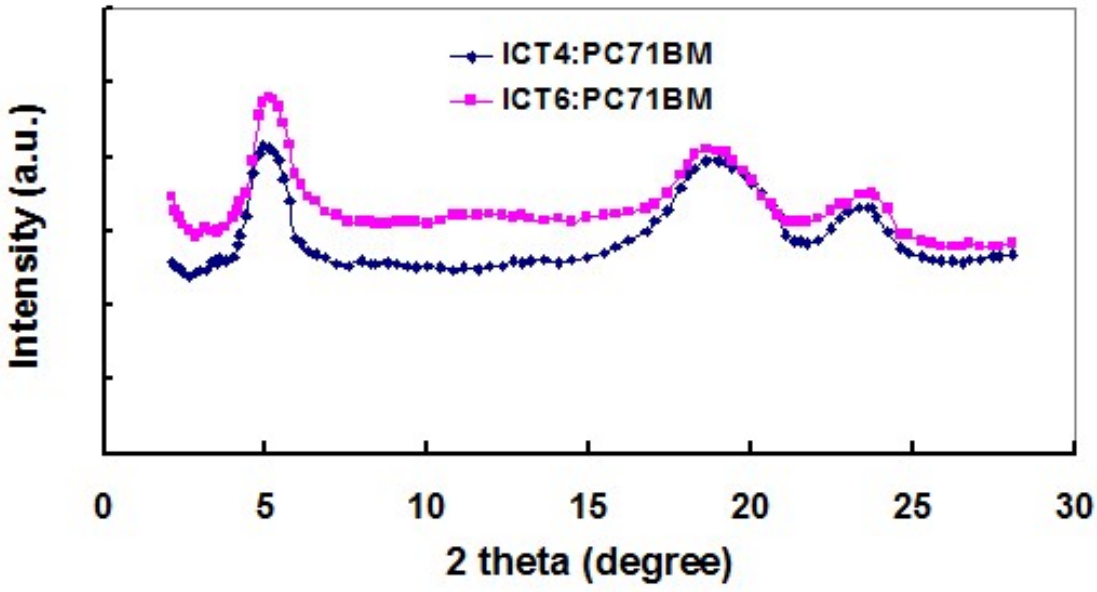


Fig. S15. X-ray diffraction of as cast **ICT4**:$PC_{71}BM$ and **ICT6**:$PC_{71}BM$ blend thin films

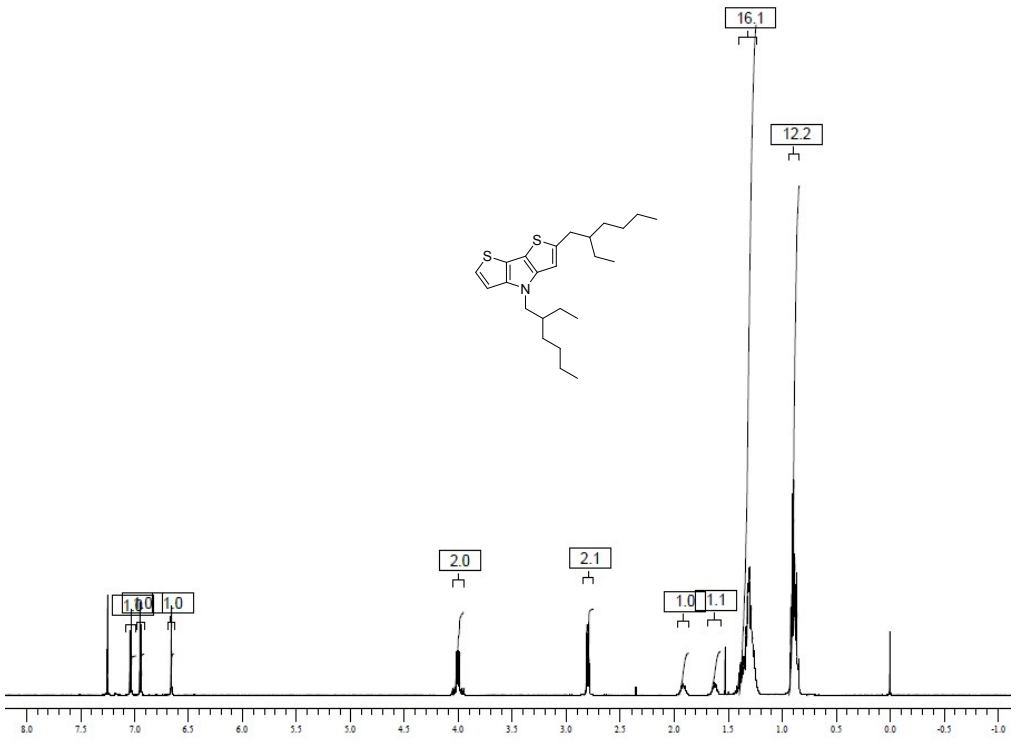


Fig. S16. ^{1}H NMR spectrum of **7**

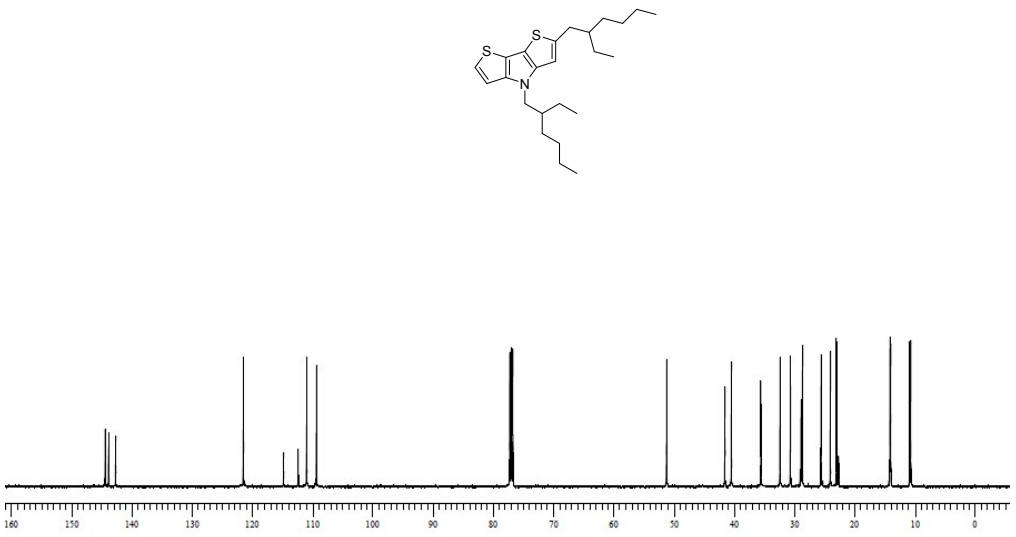


Fig. S17. ^{13}C NMR spectrum of **7**

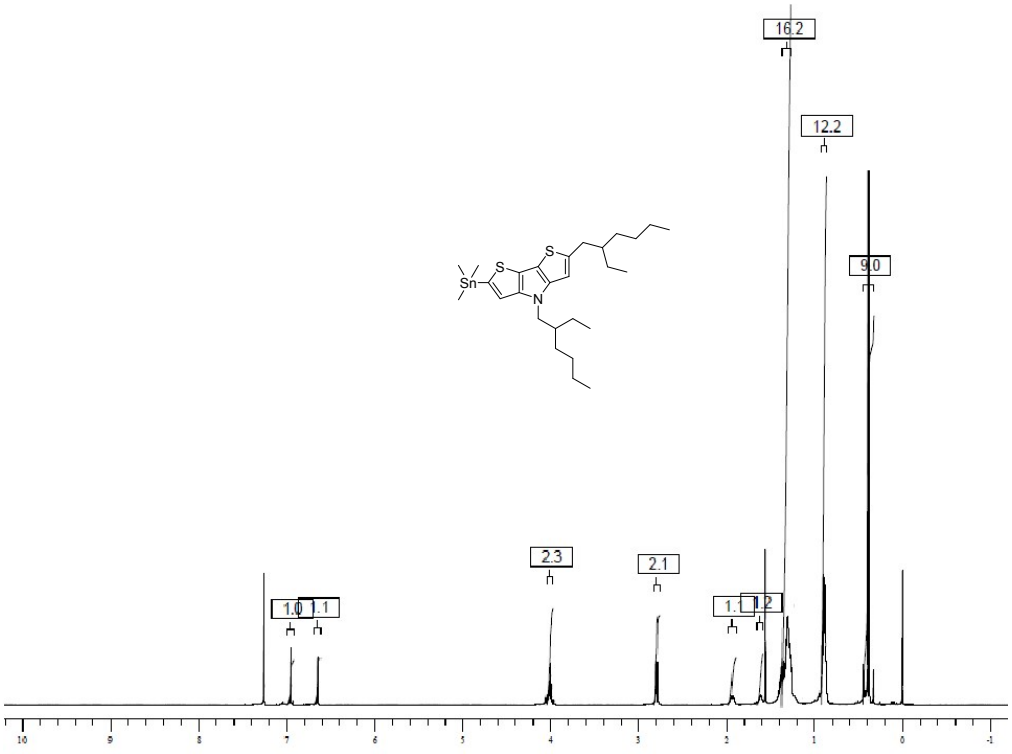


Fig. S18. ^{1}H NMR spectrum of **8**

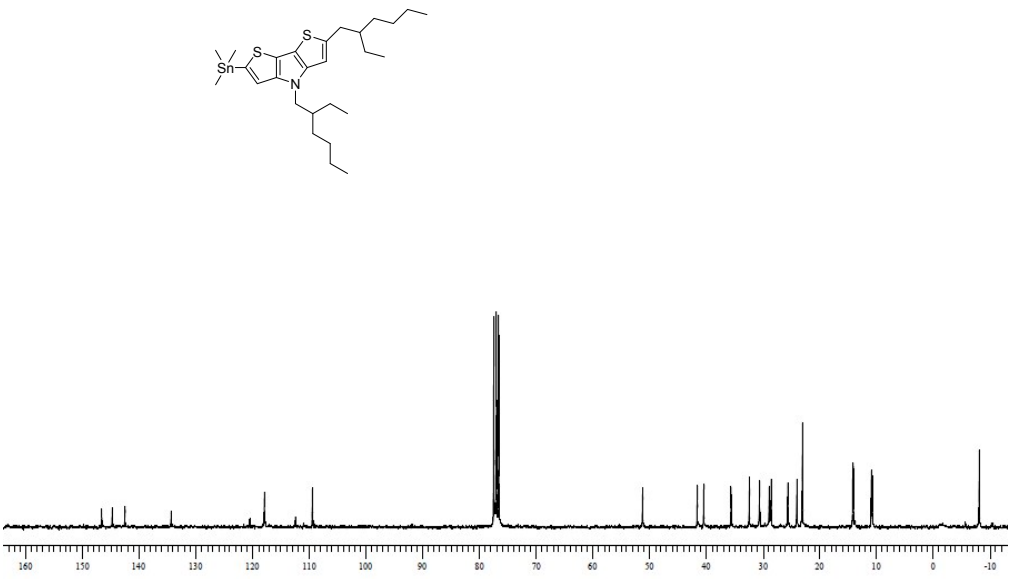


Fig. S19. ^{13}C NMR spectrum of **8**

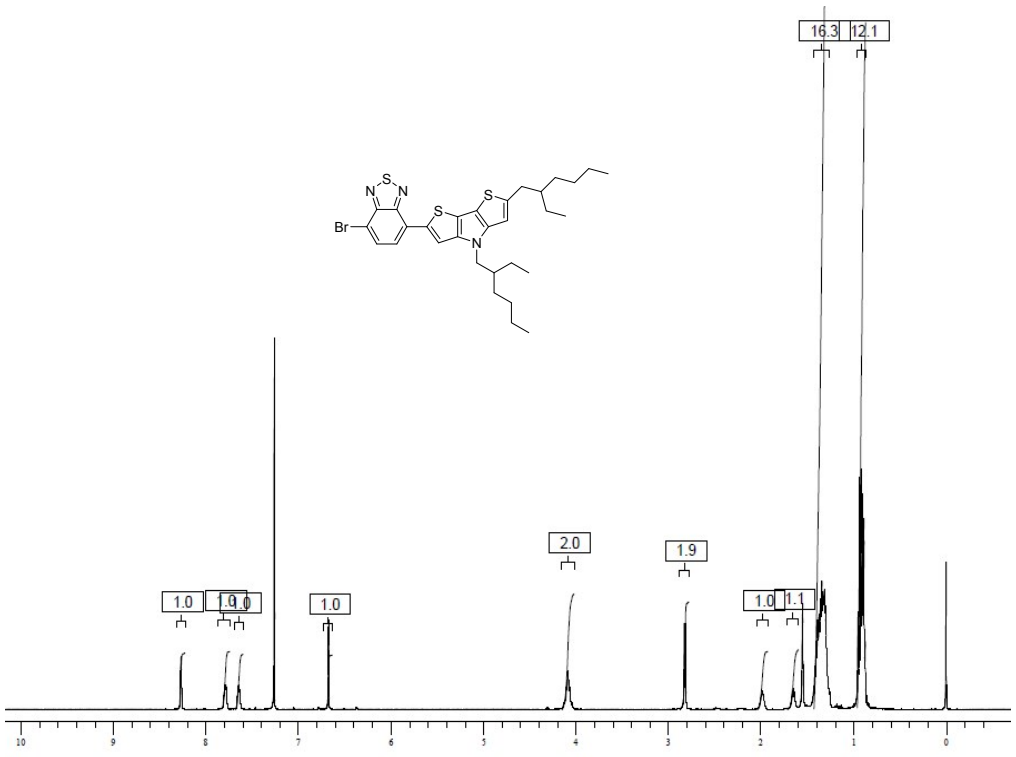


Fig. S20. ^{1}H NMR spectrum of **9**

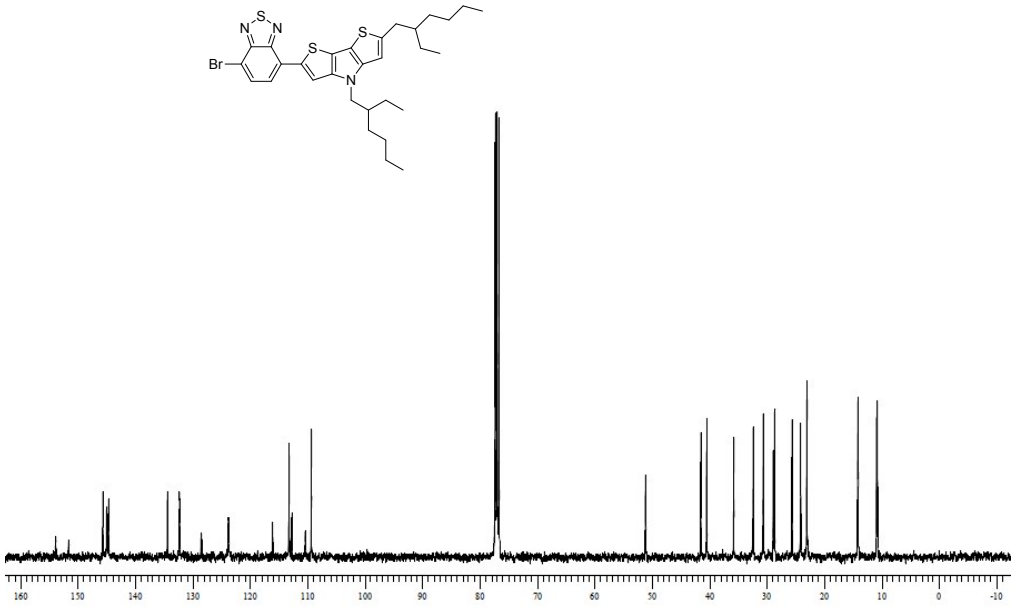


Fig. S21. ^{13}C NMR spectrum of **9**

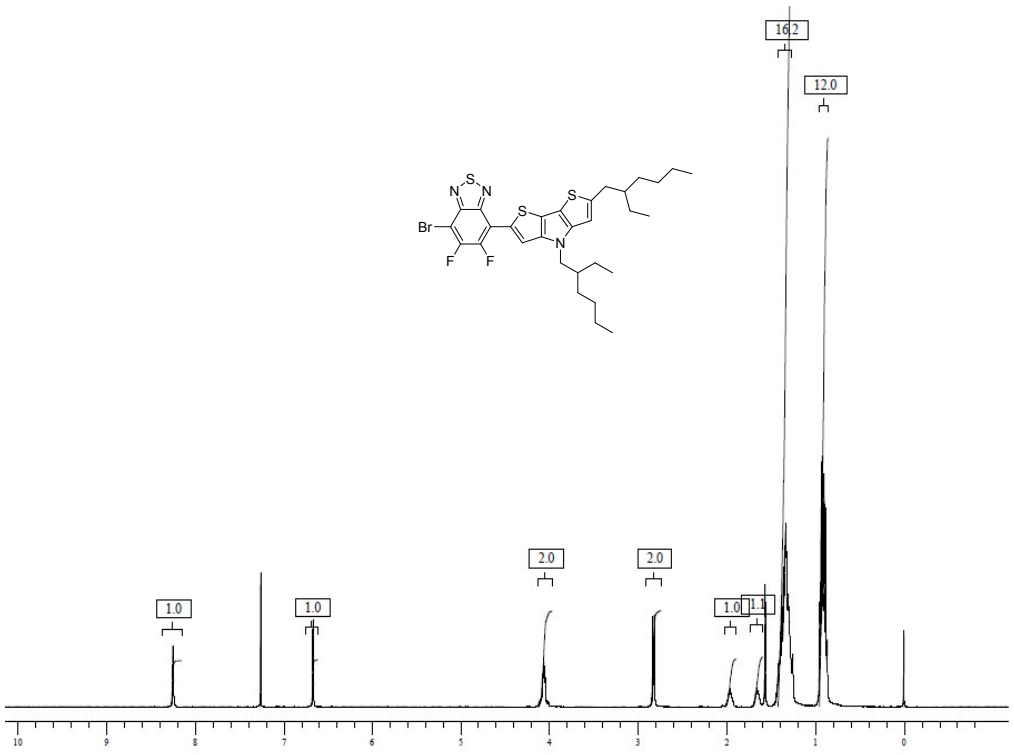


Fig. S22. ^{1}H NMR spectrum of **10**

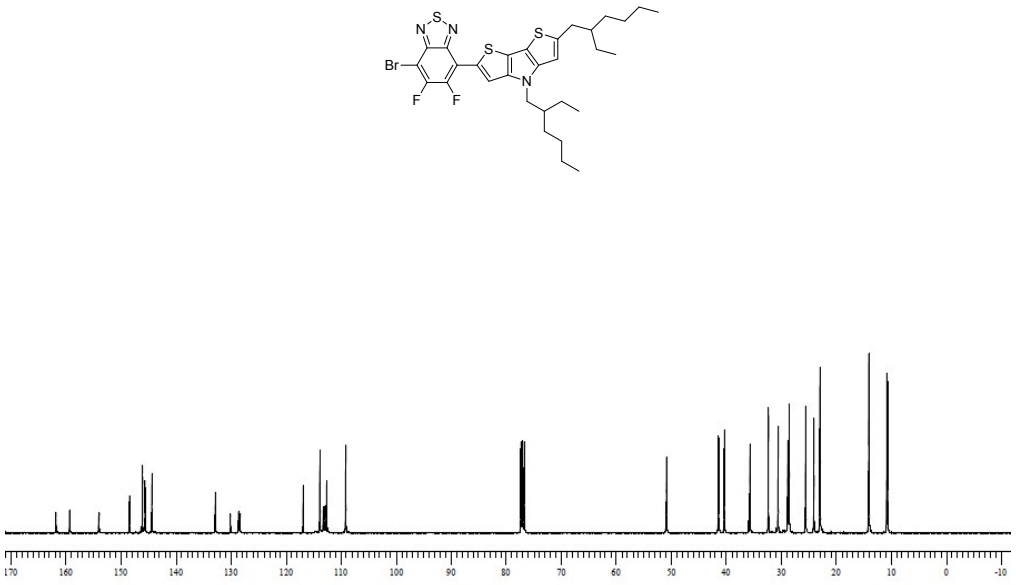


Fig. S23. ^{13}C NMR spectrum of **10**