

Supplementary Information

Molecular ordering of A(D-A'-D)₂-based organic semiconductors through hydrogen bonding after simple cleavage of tert-butyloxycarbonyl protecting group[†]

Cuc Kim Trinh^{a,‡}, Hong-Joon Lee^{a,‡}, Jin-Woo Choi^a, Mohamed Shaker^{a,b}, Wonbin Kim^a and Jae-Suk Lee^{*a}

^a School of Materials Science & Engineering, Research Institute for Solar and Sustainable Energies (RISE), Heeger Center for Advanced Materials, Advanced Photonics Research Institute (APRI), Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea. E-mail: jslee@gist.ac.kr

^b Chemistry Department, Faculty of Science, Tanta University, Tanta 31527, Egypt

Supplementary Information

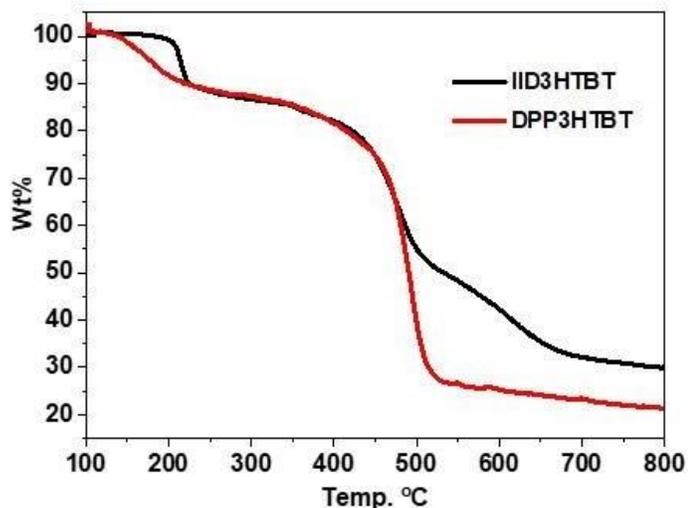
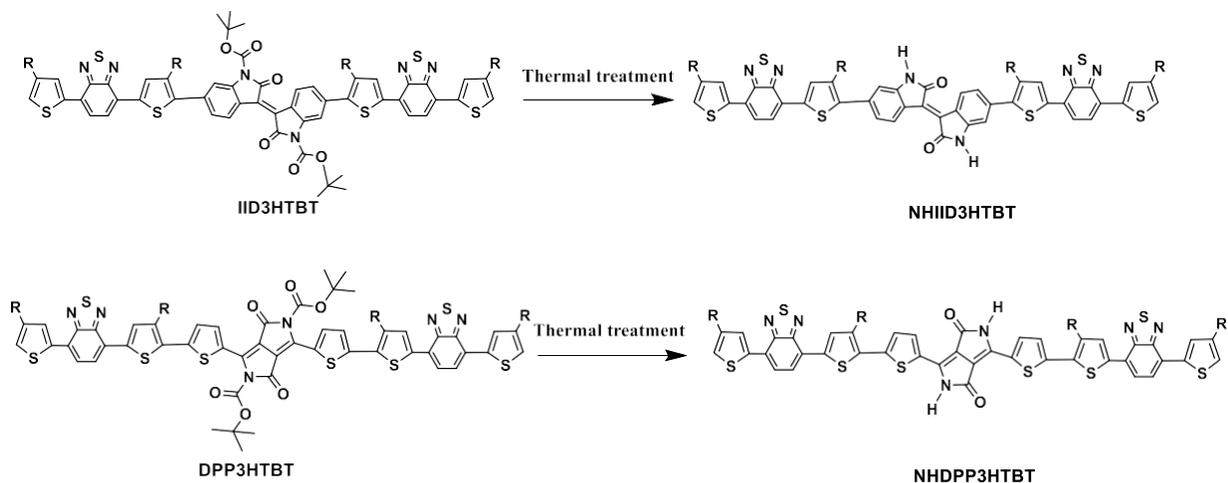


Fig. S1 TGA curves of IID3HTBT and DPP3HTBT at a heating rate of 10 °C/min in N₂. After the first decomposition at approximately 200 °C, the second decomposition peak at approximately 400 °C appeared for both of the small molecules, which indicates the molecules are thermally stable after the t-Boc groups are removed. In general, TGA revealed that the t-Boc groups in the two small molecules were removed at 200 °C, which allows the formation of H-bonds, increasing the crystallinity and improving the hole mobility in the devices.



Scheme S1 Chemical structures of IID3HTBT and DPP3HTBT after thermal decarboxylation

Supplementary Information

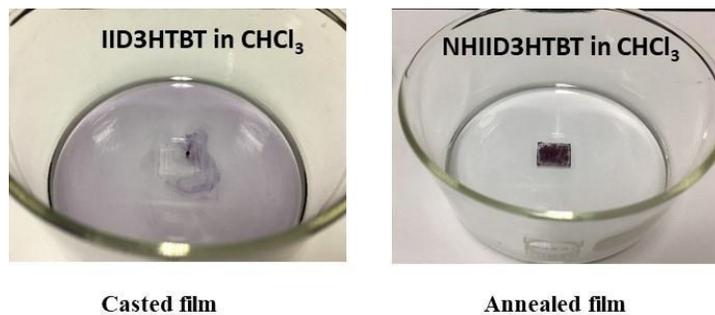


Fig. S2 Solvent resistant properties of IID3HTBT drop-casted thin films before and after thermal treatment in CHCl_3 . After thermal annealing at 200 °C for 30 min, due to the strong intermolecular interactions of N-H...O=C, the resulting annealed films were insoluble in most common solvents such as chloroform, DMSO, dichloromethane.

Supplementary Information

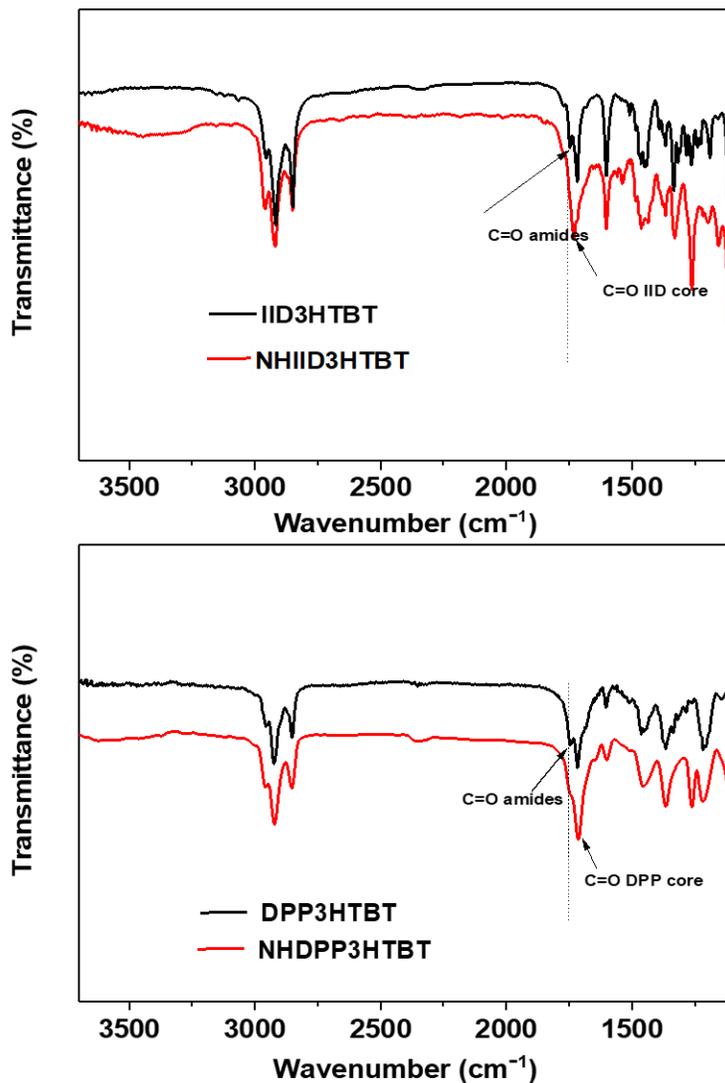


Fig. S3 FT-IR spectra of IID3HTBT and DPP3HTBT before and after thermal decarboxylation. The peak attributable to the C=O group of t-Boc at $\sim 1700\text{ cm}^{-1}$ disappeared after thermal treatment at $200\text{ }^{\circ}\text{C}$ for 30 min. This proves that the t-Boc groups were removed completely. Moreover, new weak peaks from the regenerated NH groups between 3200 and 3450 cm^{-1} appeared related to the formation of hydrogen bonds (N-H...O=C) after thermal decarboxylation.

Supplementary Information

Table S1 Optical and electrochemical properties of IID3HTBT and DPP3HTBT.

Materials	UV-vis Absorbance				Cyclic Voltammetry	
	Solution		Film		E_{HOMO} (ev)	E_{LUMO} (ev)
	λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	$E_{\text{g}}^{\text{opt}}$ (ev)		
IID3HTBT	601	698	800	1.55	-5.82	-3.91
NHIID3HTBT		549	736	1.68	-5.84	-3.88
DPP3HTBT	482	528	684	1.81	-5.84	-3.79
NHDPP3HTBT		520	679	1.82	-5.81	-3.81

Supplementary Information

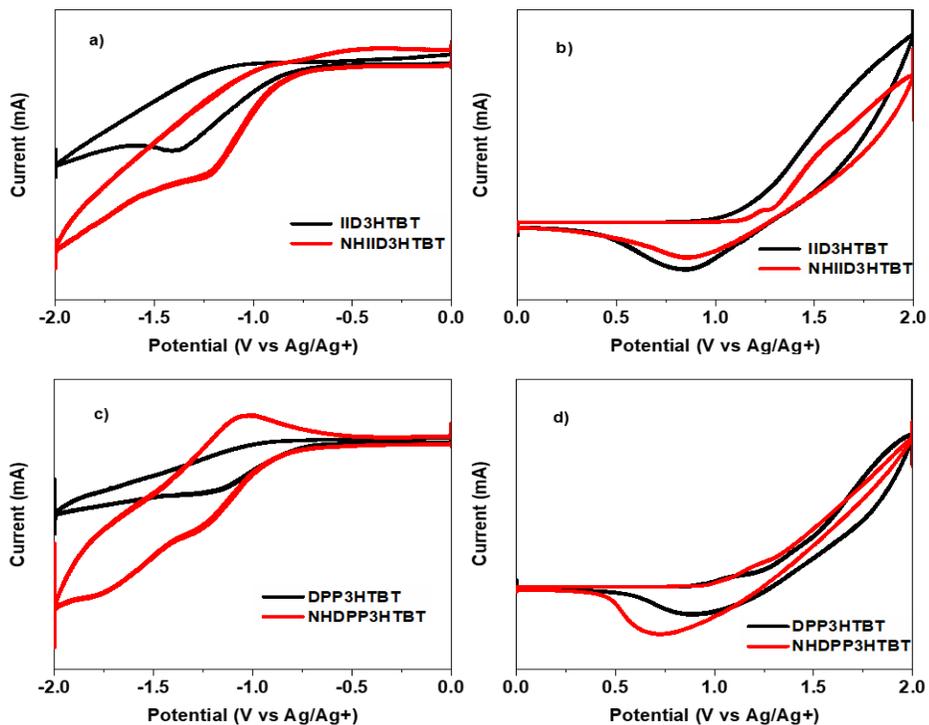


Fig. S4 Cyclic voltammograms of small molecules before and after thermal decarboxylation. a) Reduction scan of IID3HTBT; b) oxidation scan of IID3HTBT; c) reduction scan of DPP3HTBT; and d) oxidation scan of DPP3HTBT. The oxidation and reduction potentials of all casted and annealed small molecules thin films on ITO glass were investigated in 0.1 M solution of TBAPF₆ in acetonitrile.

Supplementary Information

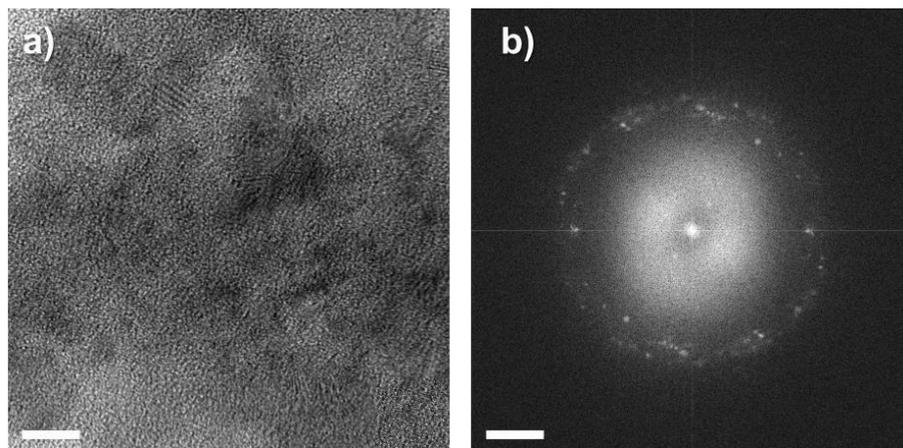


Fig. S5 a) HRTEM and b) FFT images of IID3HTBT. Scale bars are 10 nm in a) and 2 nm^{-1} in b).

Supplementary Information

Hole-only device

The charge transportation characteristics of the synthesized small molecules were evaluated in hole-only devices. The structure of hole only devices were ITO/ PEDOT:PSS/ small molecules/ MoO₃/ Ag. As an example, Fig. S6 a) presents the current density–voltage (J–V) characteristics of the fabricated hole only devices with an IID3HTBT layer without thermal annealing.

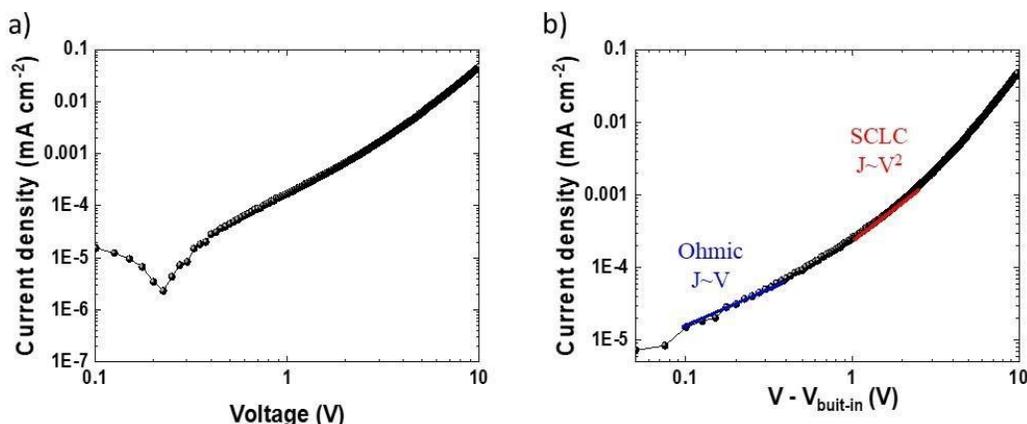


Fig. S6 a) J-V characteristic of IID3HTBT without thermal annealing. b) J-V curve corrected by the built-in potential.

However, the J-V characteristic of hole only device does not show its minimum current value at 0 V. While our hole only device is using ITO and Ag as electrode for each side of the hole only device, asymmetry electrode generated internal built-in fields inside the hole only device.^{1,2} Therefore, fitting process consisted correction term " $V_{\text{built-in}}$ ". The current level of hole only device will be minimized when the built-in potential counterbalanced by external field. Therefore, we assumed $V_{\text{built-in}}$ of 0.22 V from the Fig. S6 a). By assuming $V_{\text{built-in}}$ of 0.22 V, the shape of the J-V curve shows proper ohmic contact at low voltage region and space-charge-limited conduction (SCLC) characteristic at high voltage region (Fig. S6 b)). This ohmic characteristic shows that PEDOT:PSS and MoO₃ were proper hole injection layer for hole only devices. Fig. S7 presents the J–V characteristics of the fabricated hole-only device with an NHIID3HTBT, DPP3HTBT, and NHDPP3HTBT layer. Finally, the mobility extraction is done by calculate the measured data with the Mott–Gurney law in the high-voltage region where current follow a quadratic dependence on $V - V_{\text{built-in}}$.^{3,4}

Supplementary Information

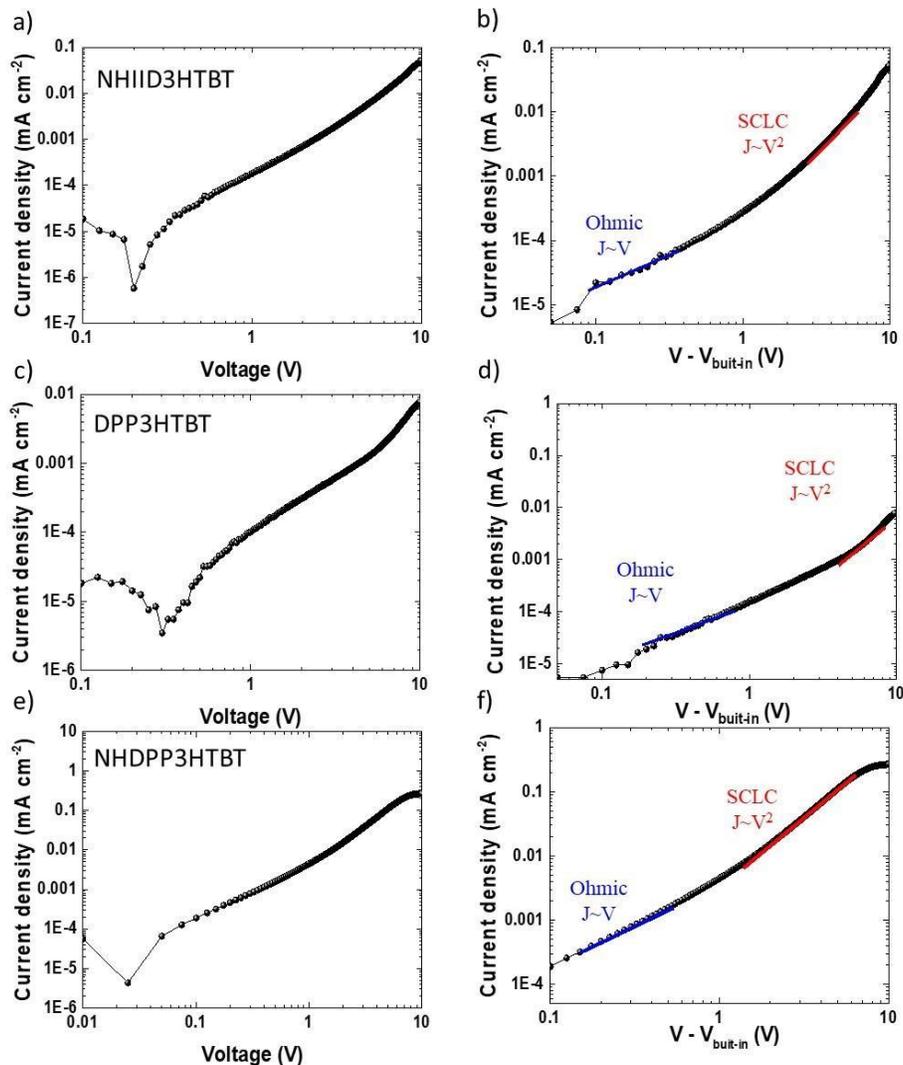


Fig. S7 J-V characteristic of NHIID3HTBT, DPP3HTBT, NHDPP3HTBT; a), c), d) are measured data and b), d), f) are corrected data by built-in potential.

Table S2 Summary of HOD characterizations of IID3HBT and DPP3HTBT.

	Hole Mobility (cm^2/Vs)	
	As casted	Annealed
IID3HTBT	2.10×10^{-6}	6.20×10^{-6}
DPP3HTBT	4.90×10^{-6}	6.10×10^{-5}

Supplementary Information

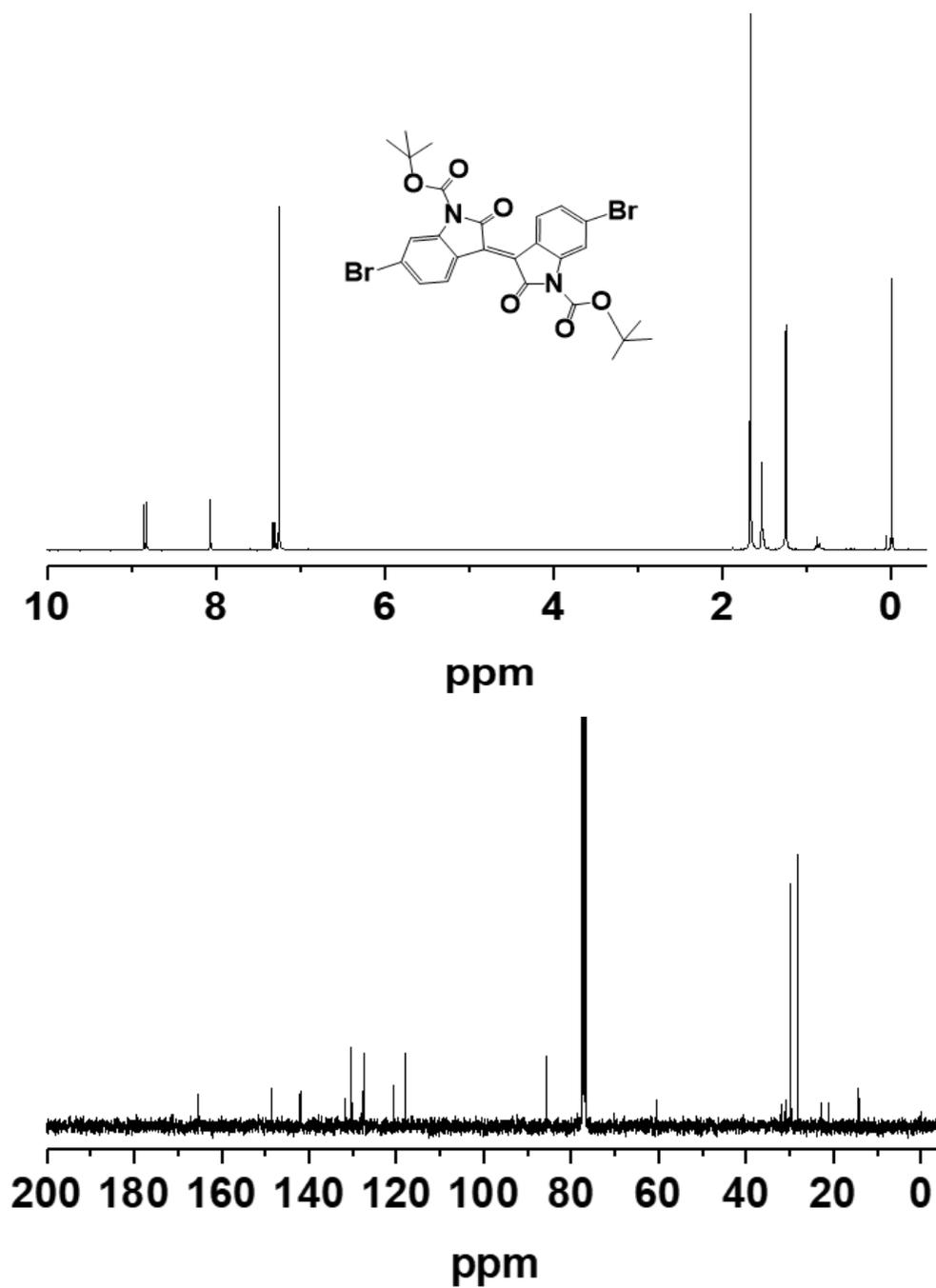


Fig. S8 ^1H and ^{13}C NMR spectrum of compound 2 in CDCl_3 .

Supplementary Information

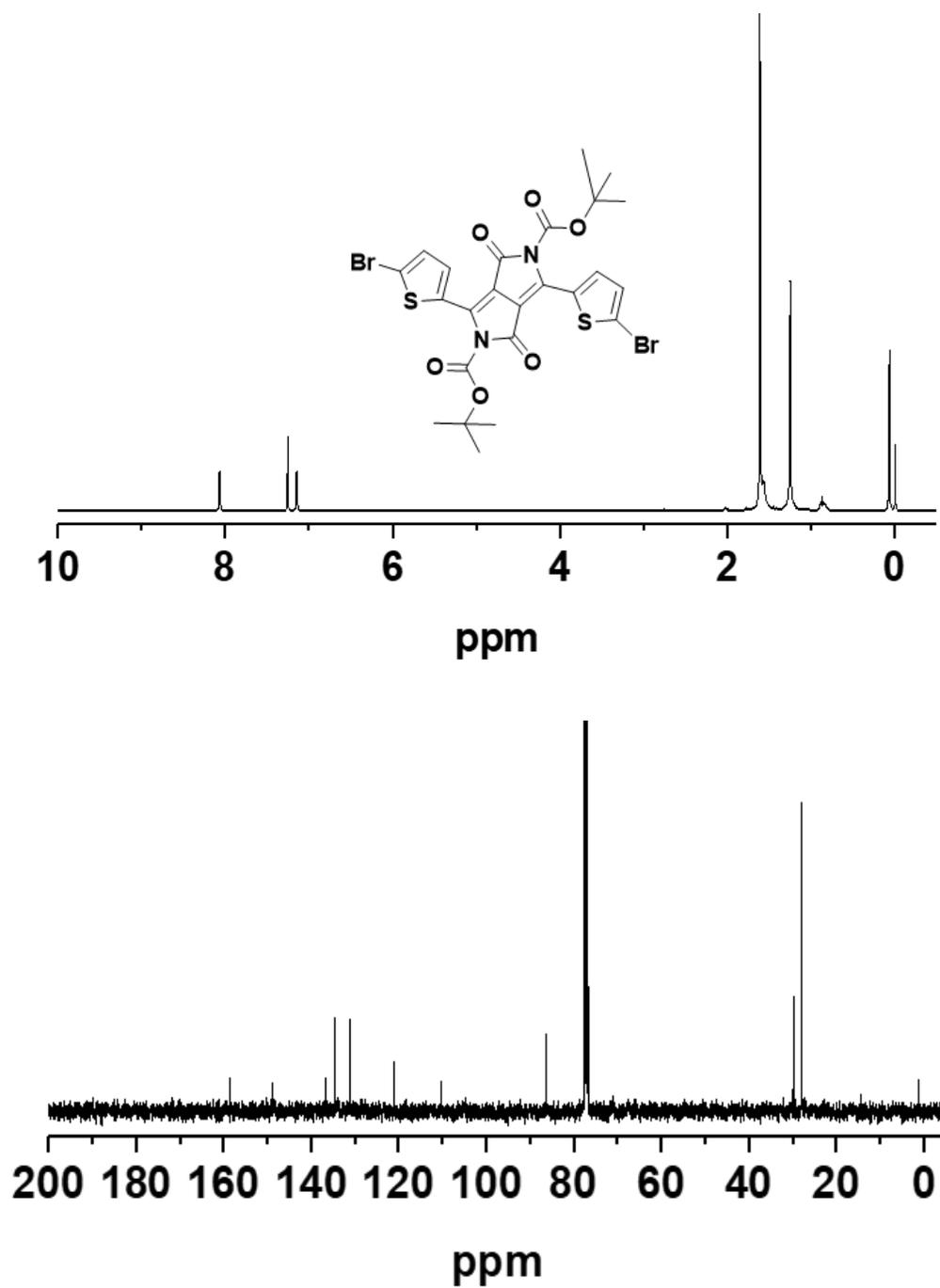


Fig. S9 ^1H and ^{13}C NMR spectrum of compound 5 in CDCl_3 .

Supplementary Information

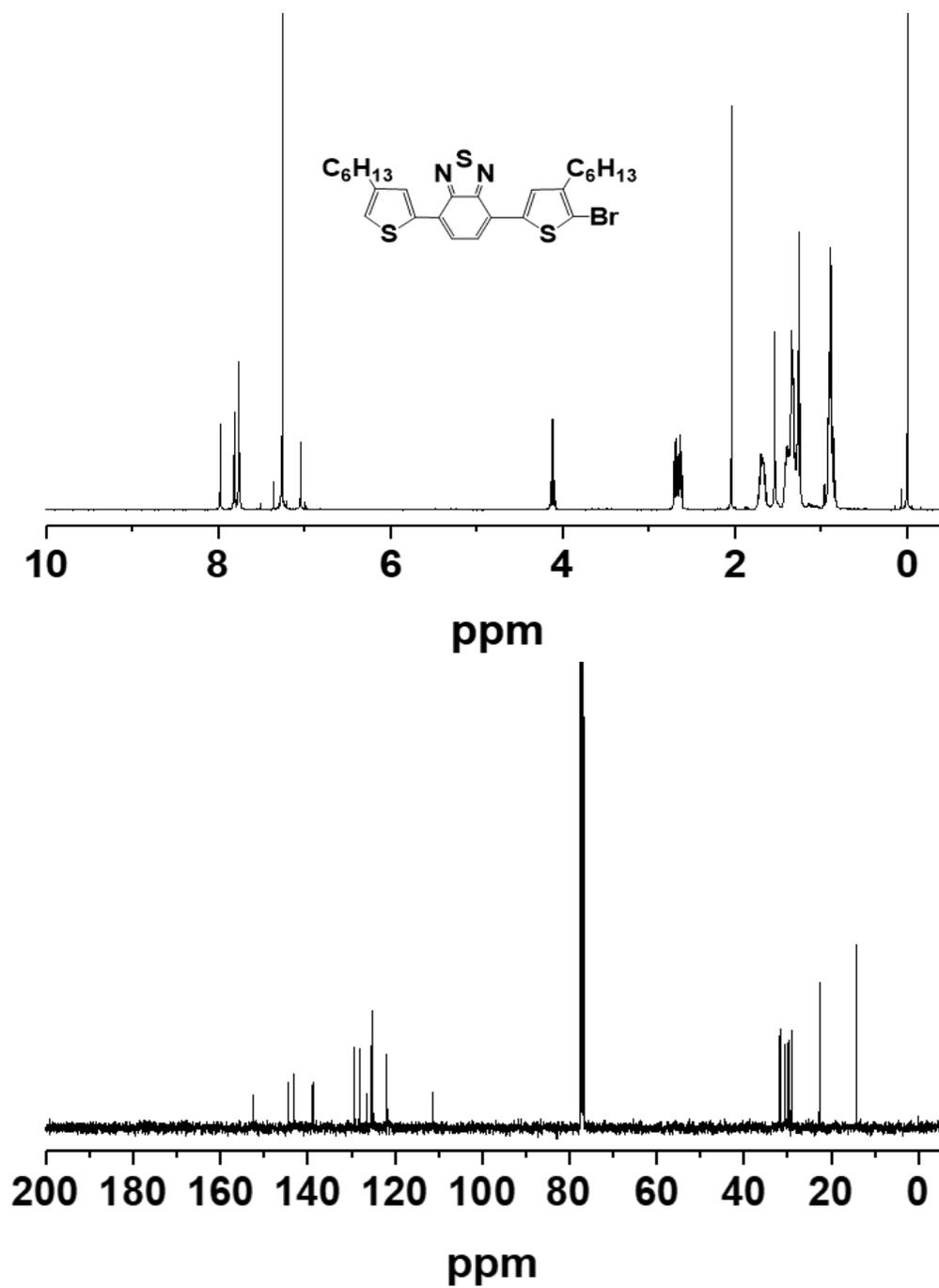


Fig. S10 ^1H and ^{13}C NMR spectrum of compound 8 in CDCl_3 .

Supplementary Information

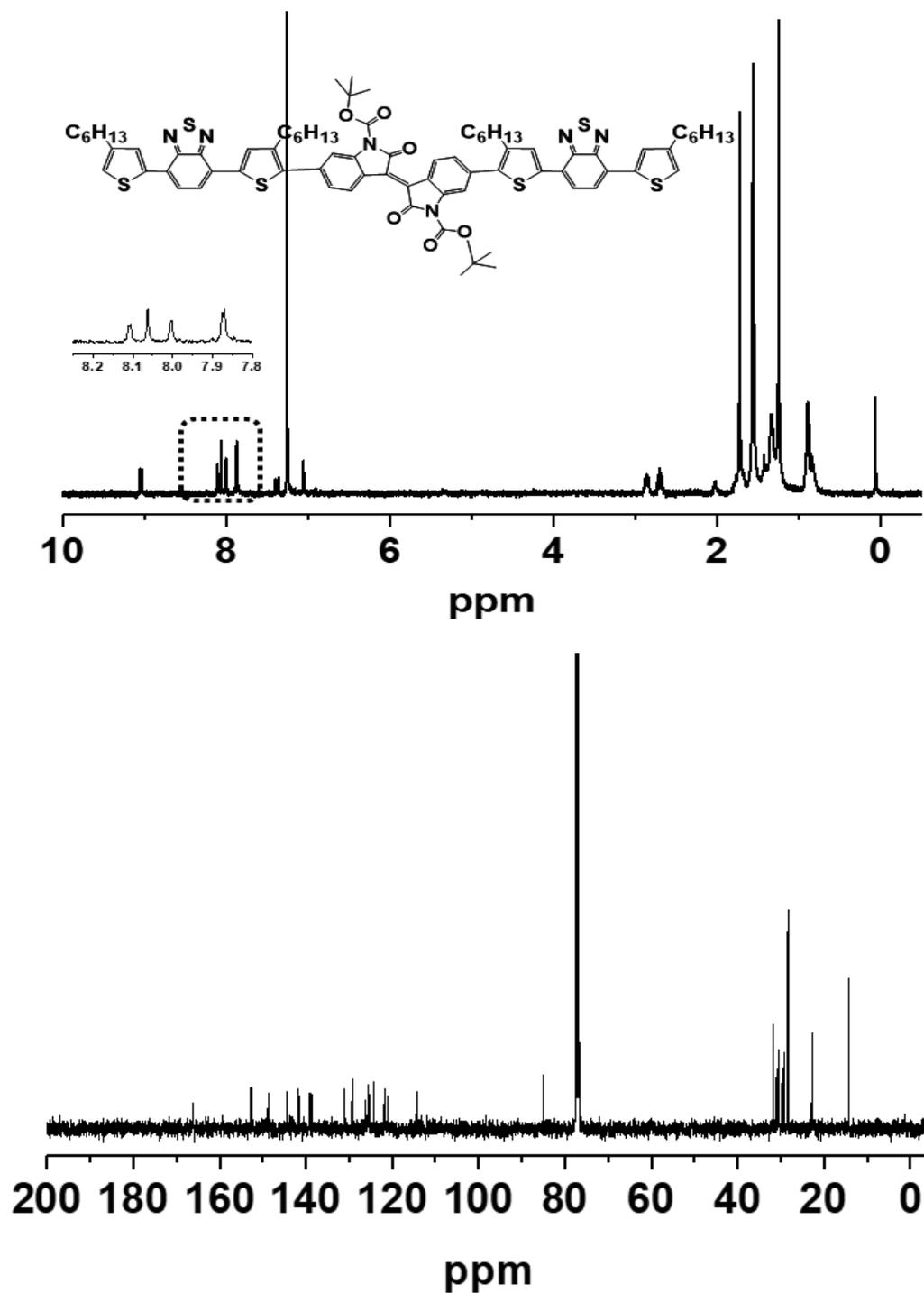


Fig. S11 ^1H and ^{13}C NMR spectrum of IID3HTBT in CDCl_3 .

Supplementary Information

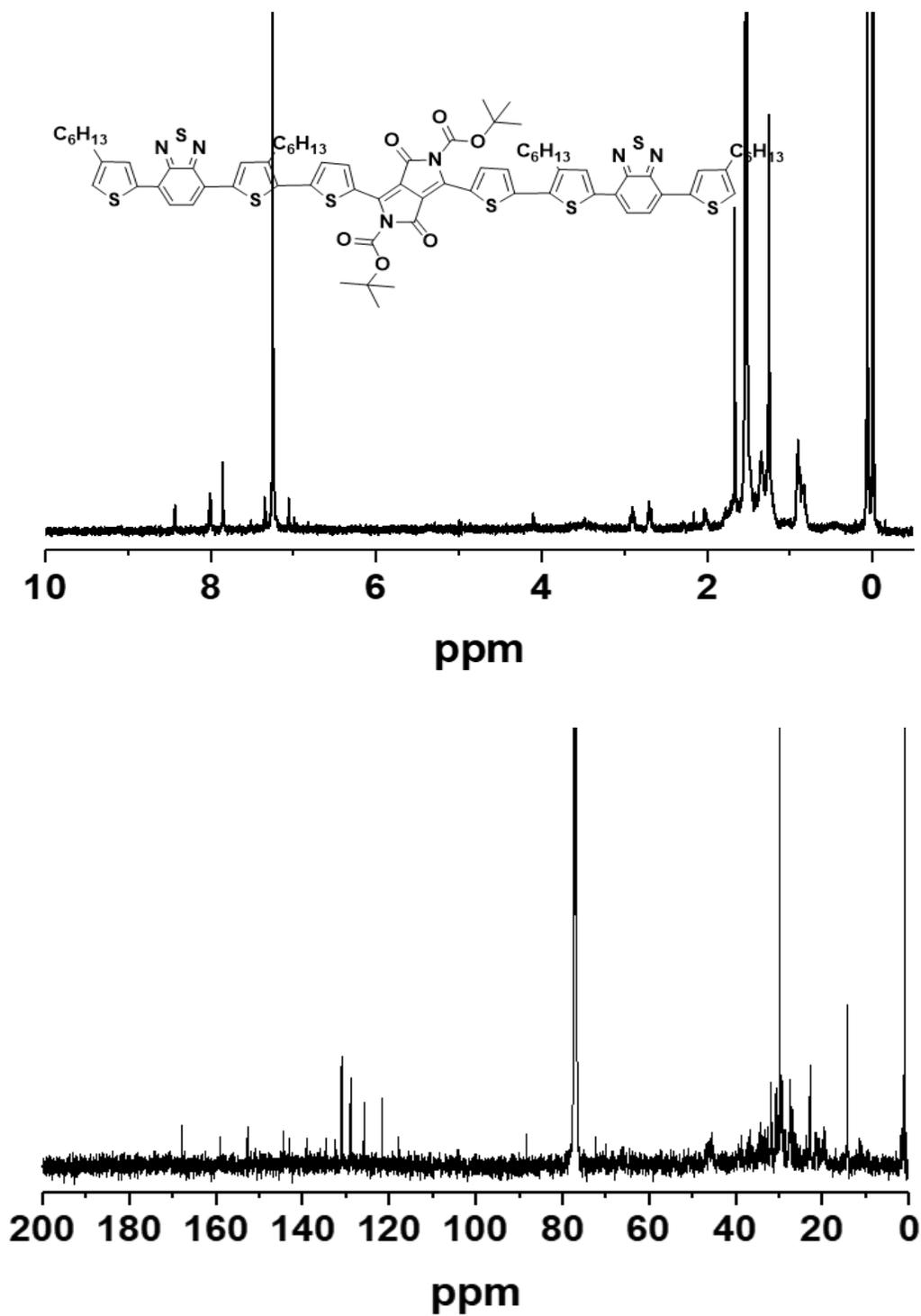


Fig. S12 ^1H and ^{13}C NMR spectrum of DPP3HTBT in CDCl_3 .

Supplementary Information

References

1. A. Kahn, N. Koch and W. Gao, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 2529
2. J. Hwang, A. Wan and A. Kahn, *Mater. Sci. Eng., R*, 2009, **64**, 1
3. M. Kiy, P. Losio, I. Biaggio, M. Koehler, A. Tapponnier and P. Gunter, *Appl. Phys. Lett.*, 2002, **80**, 1198
4. W. Chandra, L. K. Ang, K. L. Pey and C. M. Ng, *Appl. Phys. Lett.*, 2007, **90**, 153505