Supporting Information

Molecular Phase Engineering of Organic Semiconductors Based on [1]benzothieno[3,2-*b*][1]benzothiophene Core

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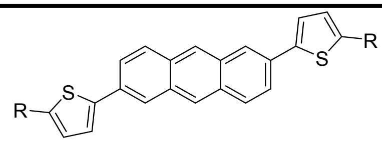
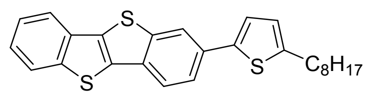
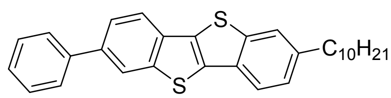
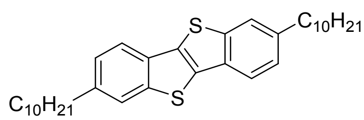
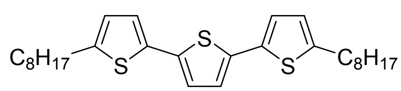
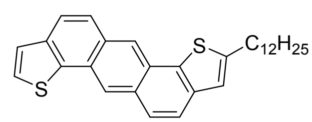
Table of Contents

1. Table S1
2. Fig.s S1-8
3. ^{1}H NMR and ^{13}C NMR of compounds **6b**, Ph-BTBT and C6-Ph-BTBT
4. References

1. Table S1

Table S1 Summary of the mobilities of a series of liquid crystalline compounds

	Structure		Mobility [$cm^2V^{-1}s^{-1}$]	Reference
DTAnt		R = H	0.063±0.006	1
DHTAnt		R= C_6H_{13}	0.50±0.045	
8-TP-BTBT			1.4±0.3	2
Ph-BTBT-10			14.7	3
C10-BTBT			3.0	4, 5
8-TTP-8			0.2	4-6
12ADT			0.68	7

2. Fig. S1-8

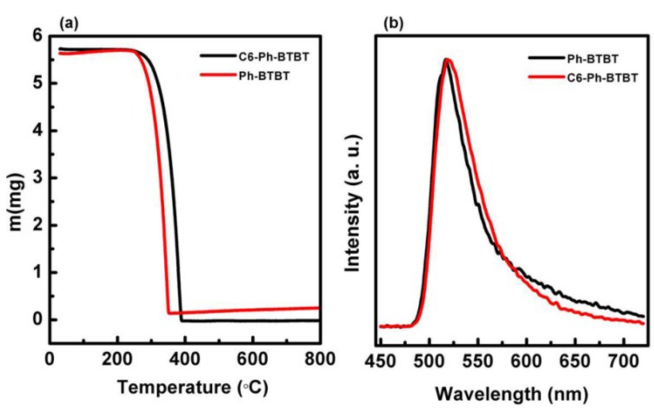


Fig. S1 TGA of Ph-BTBT and C6-Ph-BTBT; (b) PL spectra of Ph-BTBT and C6-Ph-BTBT in CH_2Cl_2

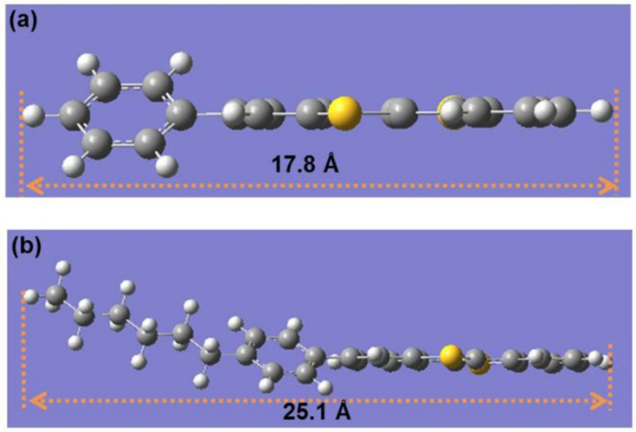


Fig. S2 The molecular length of Ph-BTBT and C6-Ph-BTBT calculated by density functional theory (DFT) level using B3LYP with 6-31+G (d, p)

Theoretical calculation: The calculations of two molecules are carried out at density functional theory (DFT)[8] level using B3LYP[9] with 6-31 + G (d, p)[10] basis set for geometrical optimization and all the calculations are performed in Gaussian 09 package.[11] The length of molecules are obtained by Multiwfn 3.3.9.[12]

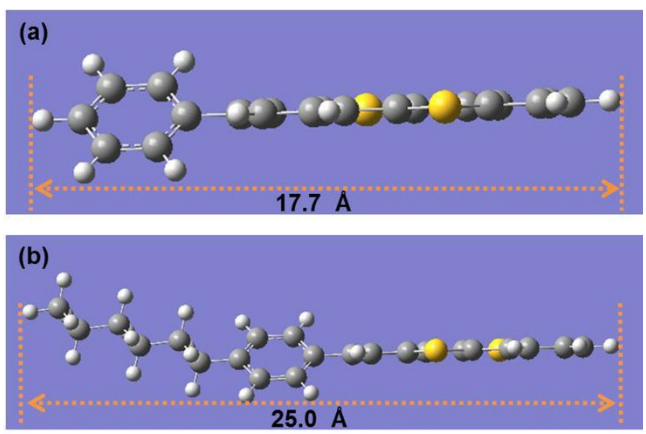


Fig. S3 The molecular length of Ph-BTBT and C6-Ph-BTBT calculated by density functional theory (DFT) level using M06-2X with 6-311 + G (d, p)

Theoretical calculation: The calculations of two molecules are carried out at density functional theory (DFT) [8] level using M06-2X [13] with 6-311 + G (d, p)[14] basis set for geometrical optimization and all the calculations are performed in Gaussian 09 package.[11] The length of molecules are obtained by Multiwfn 3.3.9.[12]

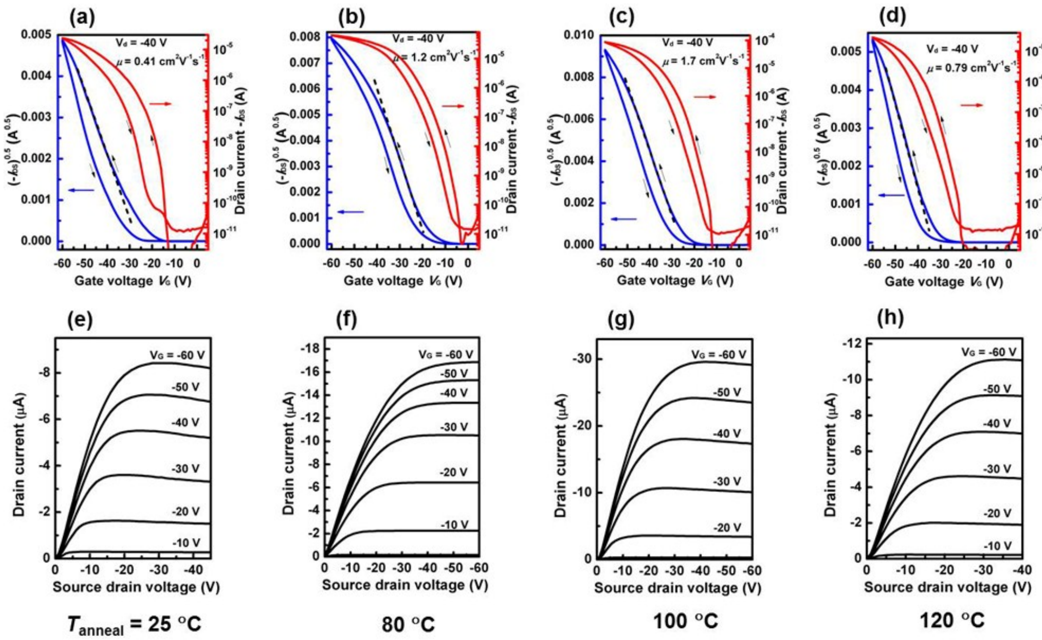


Fig. S4 Transfer and output curves of OTFTs of C6-Ph-BTBT films grown on an OTS-coated substrate at T_{sub} = 25 °C. Then the devices thermaly annealed at 25 °C (a, e),80 °C(b, f), 100 °C(c, g) and 120 °C(d, h),. a),b),c) and d) I_{DS} – V_G characteristics Curves; e), f), g) and h) I_{DS} - V_{DS} characteristics curves

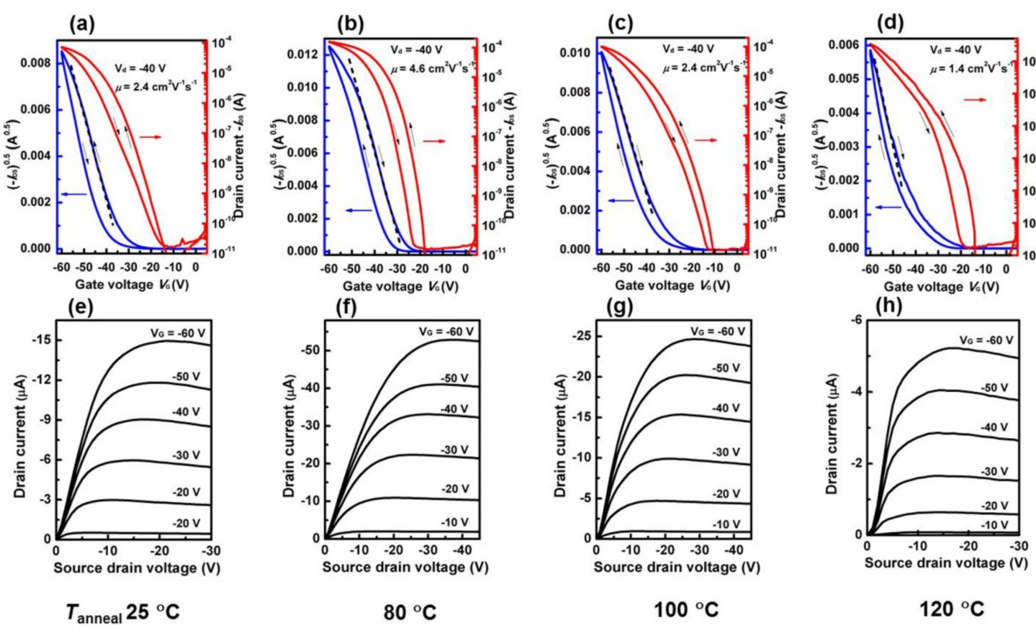


Fig. S5 Transfer and output curves of OTFTs of C6-Ph-BTBT films grown on an OTS-coated substrate at T_{sub} = 100 °C. Then the devices thermaly annealed at 25 °C (a, e), 80 °C (b, f), 100 °C (c, g) and 120 °C (d, h); (a), (b), (c) and (d) I_{DS} – V_G characteristics Curves; (e), (f), (g) and (h) I_{DS} - V_{DS} characteristics curves

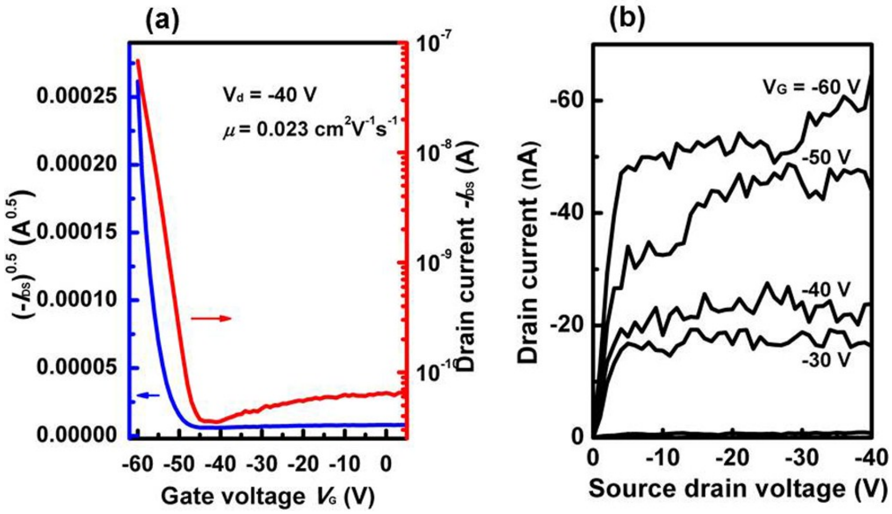


Fig. S6 Device performance of Ph-BTBT-based OTFTs substrate at T_{sub} = 25 °C. (a) transfer characteristics (I_D versus V_{GS}), (b) Output characteristics (I_D versus V_{DS})

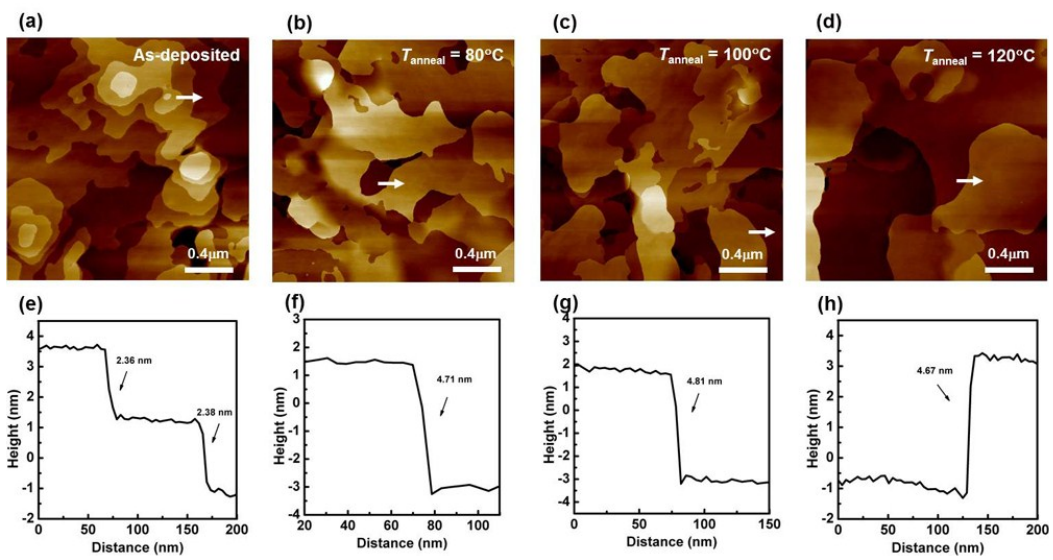


Fig. S7 AFM of polycrystalline C6-Ph-BTBT thin films (a) as-deposited, annealed at 80 ˚C (b), 100 ˚C (c) and 120 °C for 10 minutes. And (e), (f), (g) and (i) cross-sectional profiles of the samples in Fig.s 2 a, b, c and d respectively. Scanning position and direction are also indicated in Fig. a, b, c and f.

Fig.s S7a, S7b, S7c and S7d show the AFM images of the as-deposited sample and after the films were annealed at 80 °C, 100 °C and 120 °C for 10 min, respectively. The surface of the thin films as deposited presents the morphology of layered crystallinity as terraced mounds, as shown in Fig. S7a. Each step height of terraces was measured to be approximately 2.37 nm (Fig. S7e). The annealed temperatures influence the morphology of thin films of C6-Ph-BTBT. Fig.s S7b-d shows the

AFM images of the thin films of C6-Ph-BTBT after annealing at 80, 100 and 120 °C, respectively. The domain size of thin films based on C6-Ph-BTBT becomes progressively larger with increasing annealing temperatures. The step height after annealing increases from ~2.35 nm to ~4.7 nm, as seen in Fig. S7f-h. This observation suggests a bilayer structure formation. We can predict that the characteristics of the OTFTs after annealing will reach a higher performance due to the uniformity of the thin-film. However, many cracks can be observed in the thin films after annealing at 120 °C. The results are consistent with OTFTs performance. (The OTFT mobility was decreased after annealing at 120 °C).

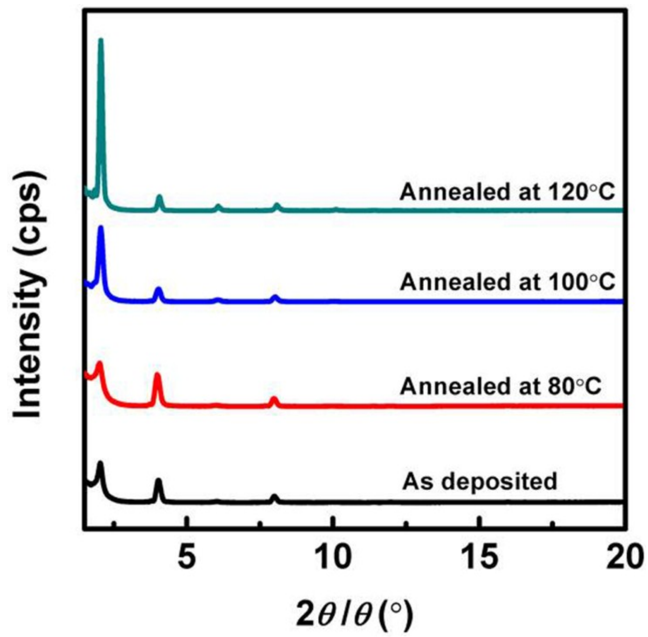
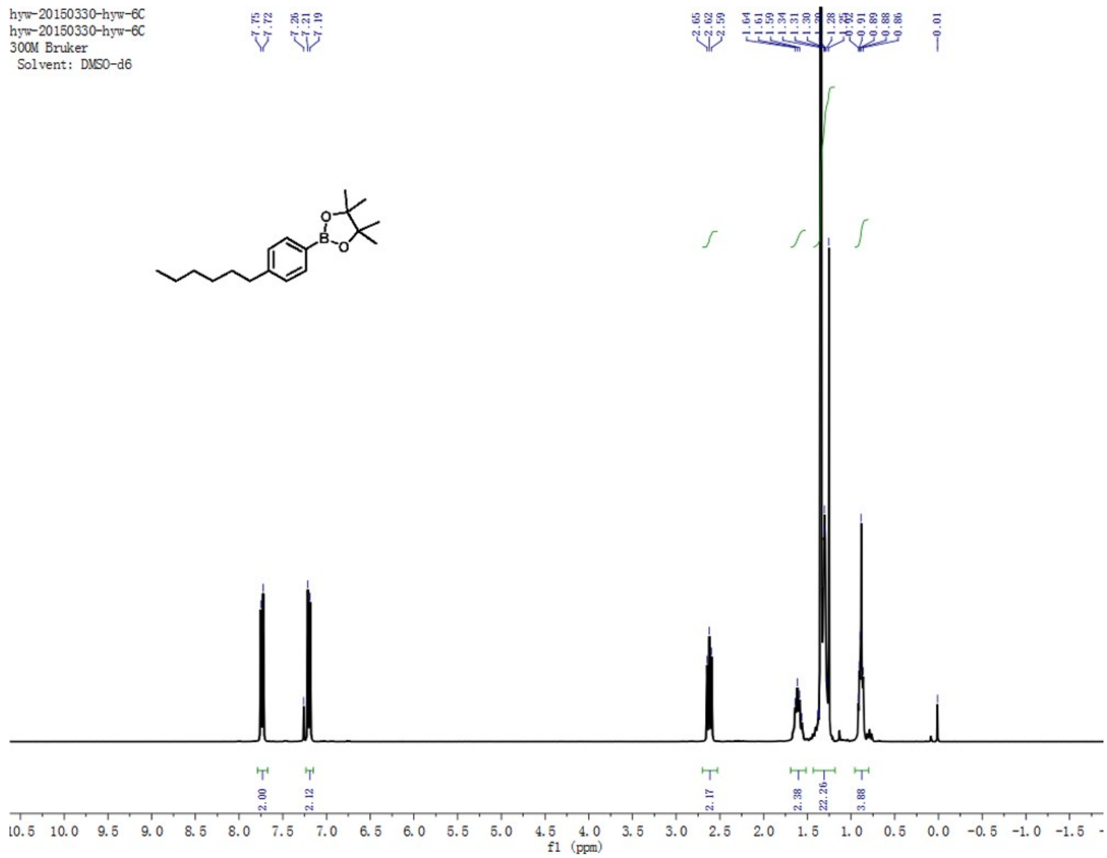
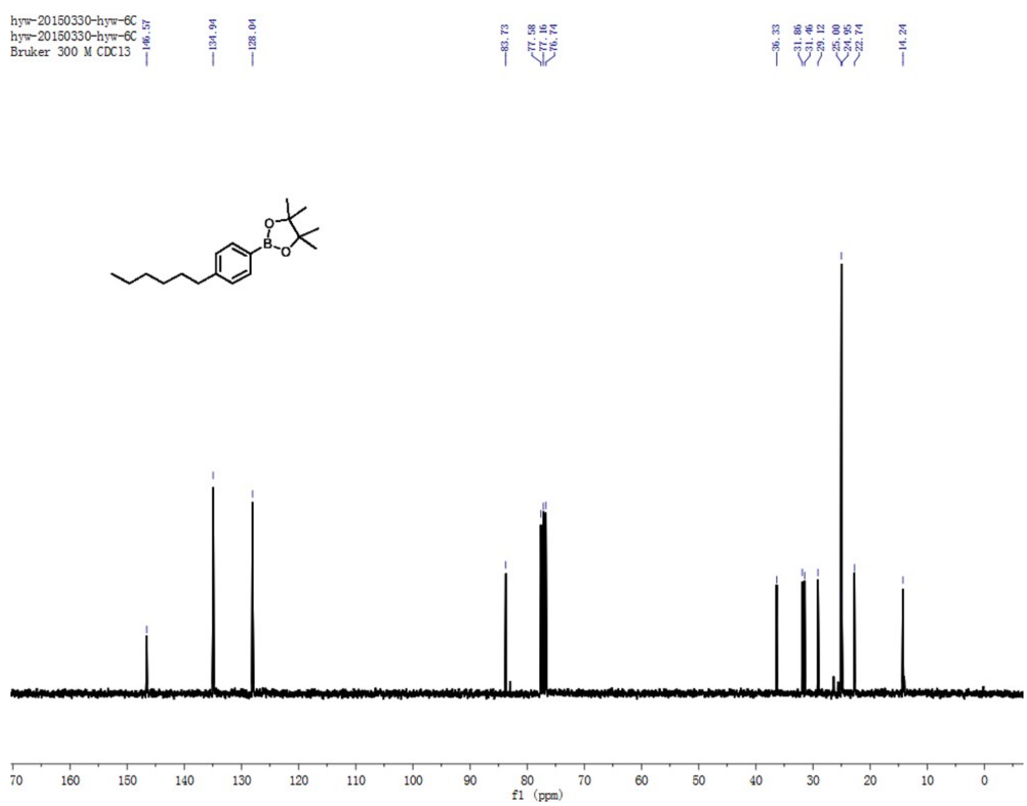


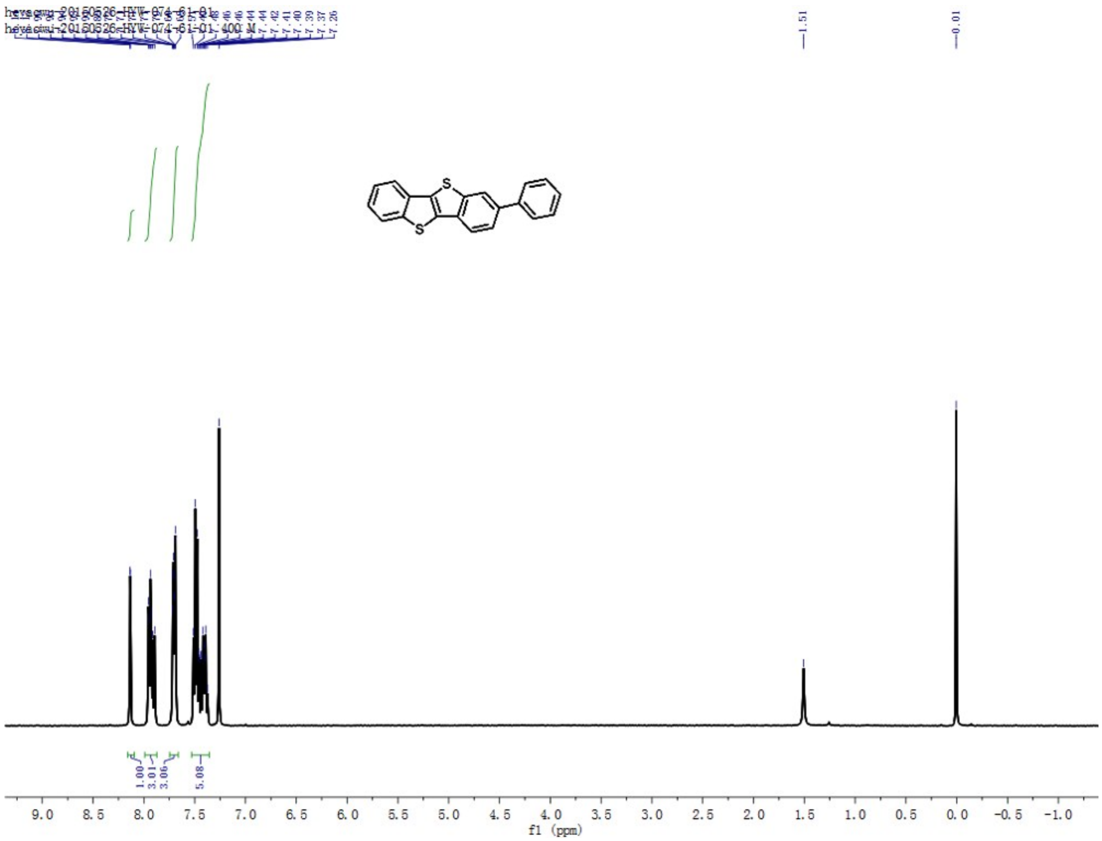
Fig. S8 XRD results for polycrystalline C6-Ph-BTBT thin films with or without annealing (80, 100 and 120 ºC).

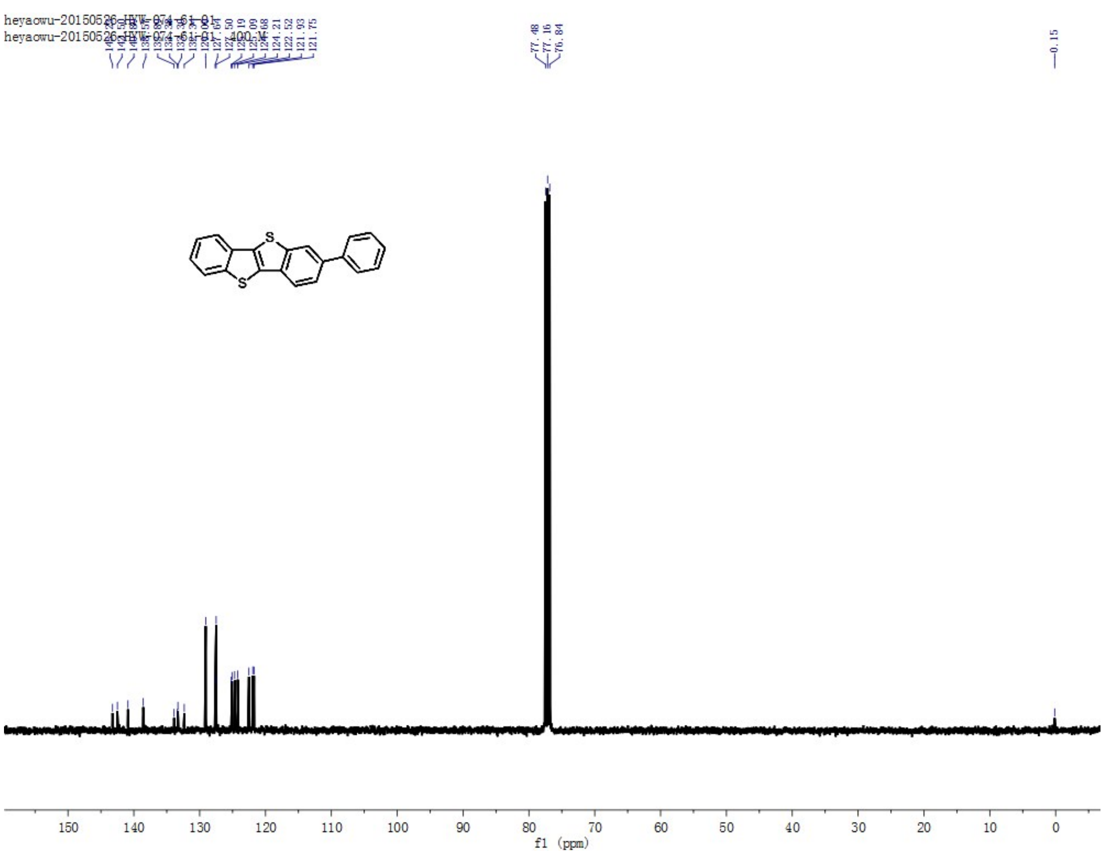
Fig. S8 shows the XRD pattern of the thin film based on C6-Ph-BTBT annealed at various temperatures. The XRD patterns of C6-Ph-BTBT show higher order reflections with the increase of annealed temperature, indicating a better ordering in films grown at higher substrate temperatures. The results are consistent with AFM morphology.

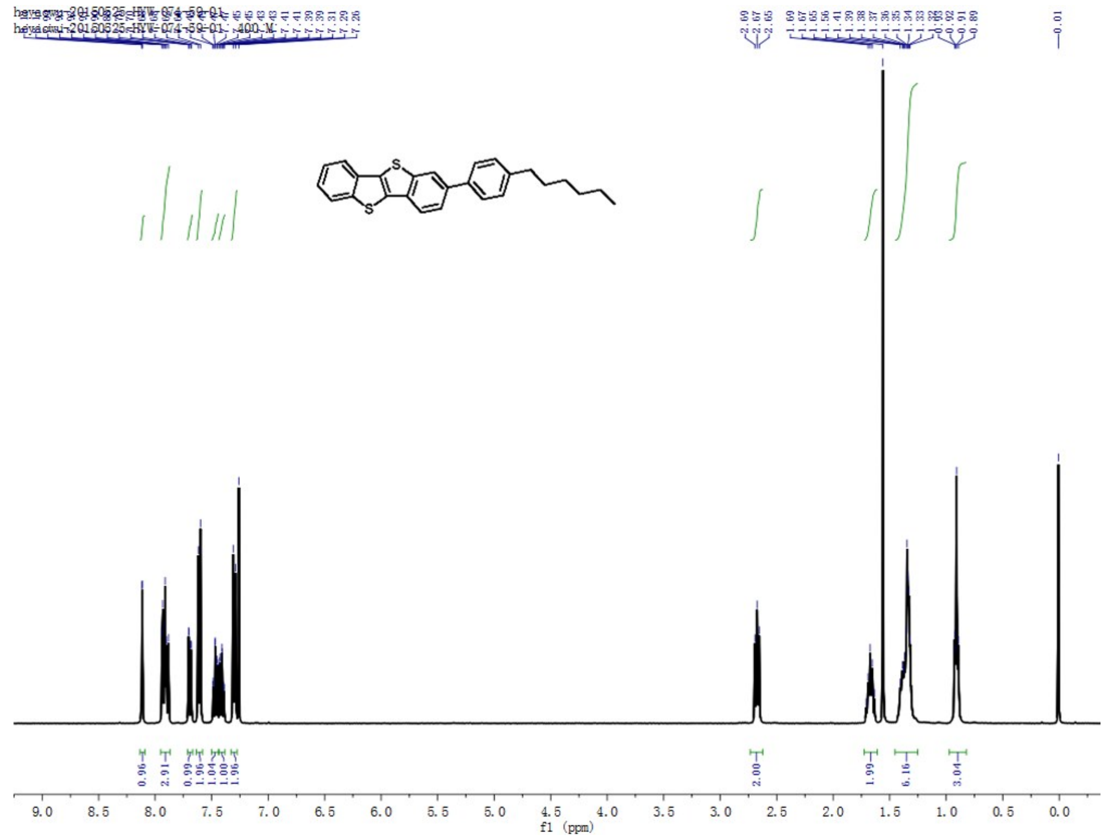
3. **^{1}H NMR and ^{13}C NMR of compounds 7b, Ph-BTBT and C6-Ph-BTBT**

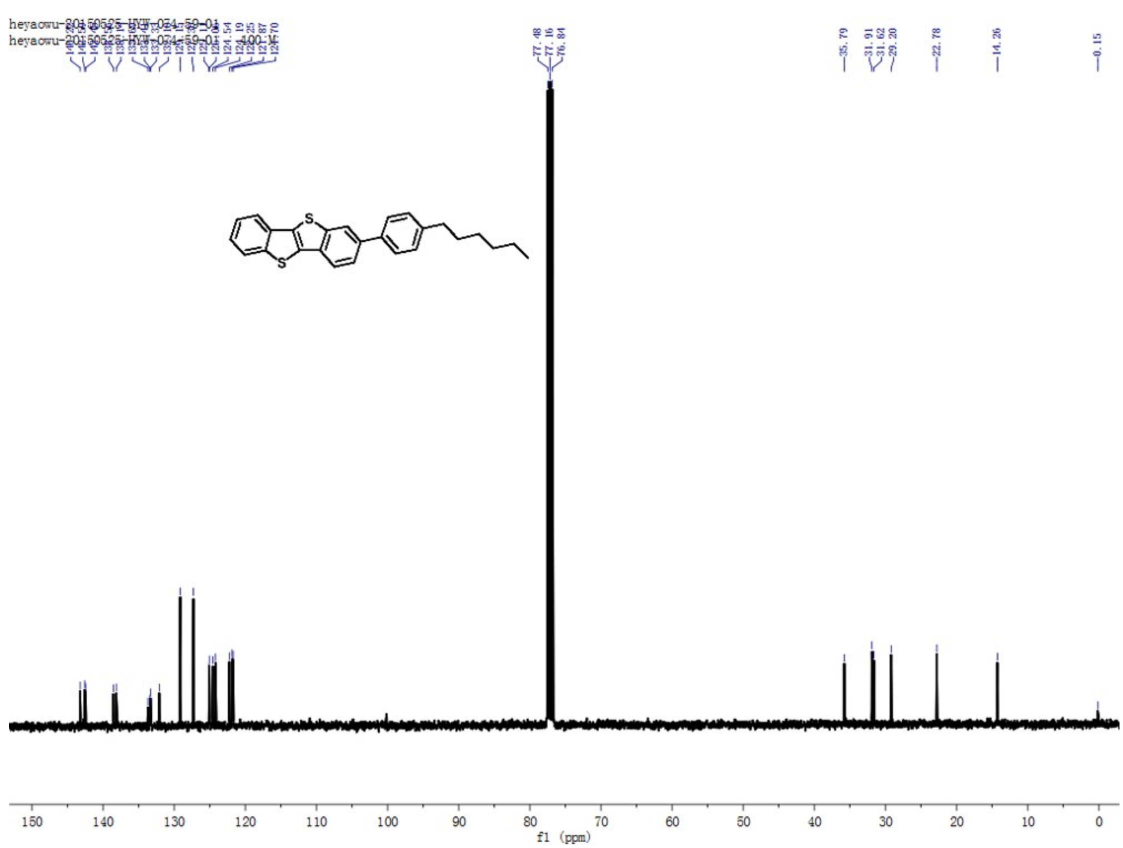












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