Supporting Information

I. Polymer synthesis

Materials. All chemicals were purchased from commercial sources (Sigma-Aldrich or Acros) and used without further purification unless otherwise stated. 4,8-Bis(alkoxy)benzo[1,2-b:4,5-b']dithiophene (1a and 1b) and 4,6-dibromothieno[3,4-b]thiophene-2-carboxylic acid (3) were synthesized according to the reported procedure[35].

Characterization. ^1H and ^{13}C NMR spectra were recorded with on a Bruker Advance III HD 500MHz NMR spectrometer using $CDCl_3$ with TMS as the internal standard. Molecular weights and molecular weight distributions of polymers were obtained using SEC with THF as an eluent at 35 ^oC and a flow rate = 1.00 mL min^{-1}. The SEC was equipped with Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å SDV columns) and connected with a differential refractive index (RI) detector (Waters, 2410) using PSS WinGPC 7.5 software. The apparent molecular weights were calculated based on linear polystyrene (PS) standards. High Resolution Mass Spectra (HRMS) were recorded on a Bruker micrOTOF II Mass Spectrometer operating in positive ESI(+) mode. Differential scanning calorimetry (DSC) was performed using a DSC-1 (Mettler Toledo), scans were performed under N_2 from -60 to +280 ^oC with heating and cooling at 10 °C/min and repeated 3 times.

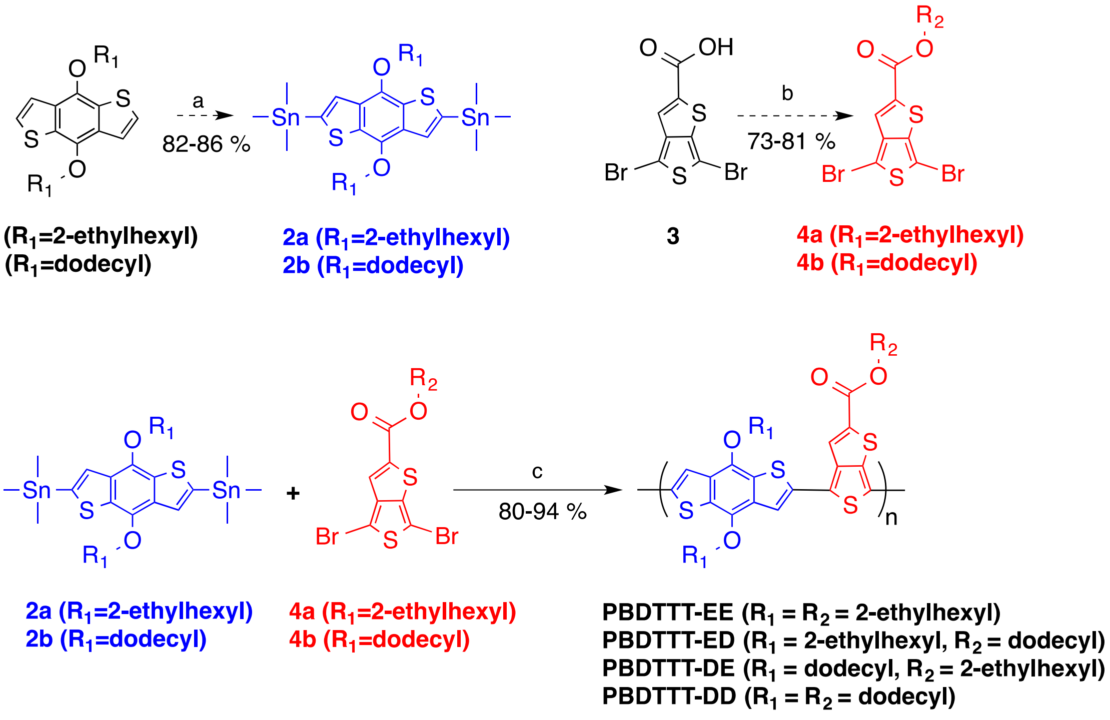

Figure S1 synthesis of PBDTTT polymers. a. n-BuLi, THF, -78 ^oC, 1h; $(CH_3)_3SnCl$, 25 ^oC, overnight; b. DCC, DMAP, 2-ethylhexanol or dodecanol, dichloromethane, overnight; c. $Pd(PPh_3)_4$, toluene:DMF (8:2 by volume), 110 ^oC, 17h.

2,6-Bis(trimethylstannyl)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (2a). Compound **1a** (2.30 g, 5.2 mmol) was added into a 50 mL three necked round bottom flask and flushed with nitrogen for 10 min. Anhydrous THF (25 mL) was added into the reaction flask and cooled to -78 ^oC. *n*-Butyllithium solution (5.2 mL, 12.9 mmol, 2.5 M in hexane) was added dropwise into the flask and the mixture was stirred for 30 min at -78 ^oC and then at room temperature for 30 min. After cooling the flask to -78 ^oC, trimethyltin chloride solution (15.6 mL, 15.6 mmol, 1 M in hexane) was added *via* a syringe in one portion and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by pouring it into 80 mL of water, extracted with diethyl ether, and dried with anhydrous $MgSO_4$. The organic solvent was removed by rotary evaporation and the crude product was recrystallized in ethanol to yield 3.40 g (86 %) of white crystals. ^1H NMR (500 MHz, $CDCl_3$, Me_4Si), δ (ppm): 7.51 (s, 2H), 4.19 (d, 4H), 1.83-1.58 (m, 8H), 1.40 (m, 10H), 1.02 (t, 6H), 0.94 (t, 6H), 0.45 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 143.2, 140.2, 133.9, 132.8, 127.9, 75.7, 40.7, 30.6, 29.3, 24.0, 23.3, 14.3, 11.4, -8.3. HRMS (ESI+) calculated for $C_{32}H_{55}O_2S_2Sn_2$: 775.1687 (M^+). Found: 775.1685 (M^+).

2,6-Bis(trimethylstannyl)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b']dithiophene (2b). Compound **1b** (3.00 g, 5.34 mmol) was added into a 50 mL three necked round bottom flask and flushed with nitrogen for 10 min. Anhydrous THF (45 mL) was added into the reaction flask and cooled to 0 °C. *n*-Butyllithium solution (5.34 mL, 13.35 mmol, 2.5 M in hexane) was added dropwise into the flask and the mixture was stirred for 30 min at 0 °C and then at room temperature for 30 min. After cooling the flask to 0 °C, trimethyltin chloride solution (16.0 mL, 16.0 mmol, 1 M in hexane) was added *via* syringe in one portion and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by pouring it into 80 mL of water, extracted with hexane, and dried with anhydrous $MgSO_4$. The organic solvent was removed by rotary evaporation and the crude product was recrystallized in ethanol to yield 3.91 g (82 %) of white crystals. ^1H NMR (500 MHz, $CDCl_3$, Me_4Si), δ (ppm): 7.51 (s, 2H), 4.29 (t, 4H), 1.88 (m, 4H), 1.56 (m, 4H), 1.45-1.22 (m, 32H), 0.88 (t, 6H), 0.44 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 143.4, 140.7, 134.3, 133.2, 128.3, 73.8, 32.1, 30.8, 30.0, 29.9, 29.8, 29.7, 29.6, 26.4, 22.9, 14.3, -8.1. HRMS (ESI+) calculated for $C_{40}H_{71}O_2S_2Sn_2$: 887.2940 (M^+). Found: 887.2974 (M^+).

2'-Ethylhexyl 4,6-dibromothieno[3,4-b]thiophene 2-carboxlate (4a). Compound **3** (0.68 g, 2.0 mmol), DCC (0.50 g, 2.4 mmol), DMAP (86 mg, 0.7 mmol), and 5 mL of dichloromethane were added into 25 mL of flask. 2-ethylhexanol (1.3 g, 10.0 mmol) was added into the reaction flask and the reaction mixture was stirred for overnight under N_2 environment. The reaction was poured into 30 mL of water, extracted with dichloromethane, and dried with anhydrous $MgSO_4$. The product was purified by silica column chromatography using hexane:dichloromethane (4:1 by volume) as an eluent mixture. The final compound was obtained as red viscous oil (0.73 g, 81 %). ^1H NMR (500 MHz, $CDCl_3$, Me_4Si), δ (ppm): 7.52 (s, 1H), 4.24 (m, 2H), 1.70 (m, 1H), 1.46-1.28 (m, 8H), 0.95 (t, 3H), 0.91 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 162.6, 145.8, 141.4, 140.7, 123.3, 102.4, 97.3, 68.6, 39.1, 30.7, 29.2, 24.1, 23.1, 14.2, 11.3. HRMS (ESI+) calculated for $C_{15}H_{19}Br_2O_2S_2$: 452.9193 (M^+). Found: 452.9191 (M^+).

Dodecyl 4,6-dibromothieno[3,4-b]thiophene 2-carboxlate (4b). Compound **3** (0.68 g, 2.0 mmol), DCC (0.50 g, 2.4 mmol), DMAP (86 mg, 0.7 mmol), and 5 mL of dichloromethane were added into 25 mL of flask. Dodecanol (1.86 g, 10.0 mmol) in 2 mL of dichloromethane was added into the reaction flask and the reaction mixture was stirred for overnight under a N_2 environment. The reaction was then poured into 30 mL of water, extracted with dichloromethane, and dried with anhydrous $MgSO_4$. The product was purified by silica column chromatography using hexane:dichloromethane (4:1 by volume) as an eluent mixture. The final compound was obtained as red viscous oil (0.74 g, 73 %). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.53 (s, 1H), 4.31 (t, 2H), 1.75 (t, 2H), 1.45-1.20 (br, 18H), 0.88 (t, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 162.6, 145.8, 141.4, 140.7, 123.3, 102.4, 97.3, 66.4, 37.8, 32.1, 29.9, 29.8, 29.7, 29.6, 29.4, 28.8, 26.1, 22.9, 14.3. HRMS (ESI+) calculated for $C_{19}H_{27}Br_2O_2S_2$: 508.9819 (M^+). Found: 508.9814 (M^+).

General Synthetic Procedure of PBDTTT polymers by Stille Reaction. The polymers were prepared by a similar procedure. Dibromo compound **4a** (0.5 mmol), bis(trimethyltin) compound **2a** (0.5 mmol), and 10 mL toluene:DMF mixture (8:2 by volume) were added into a 50 mL three-necked round-bottom flask under an inert atmosphere and stirred for 20 min. $Pd(PPh_3)_4$ catalyst (23 mg, 0.02 mmol) was added into the reaction mixture and flushed with nitrogen for another 20 min. The reaction temperature was increased slowly to 110 °C and stirred for 17 h under an inert gas atmosphere. The reaction solution was cooled to room temperature and precipitated by pouring into 150 mL of methanol. The suspension was filtered through a Soxhlet thimble, and then was extracted with methanol and further with hexane for 24 h each. The residue was then extracted using chloroform. The polymer was recovered as solid from the chloroform fraction by rotary evaporation and the solid was dried under vacuum for overnight. ^1H NMR, and molecular weight of polymers by GPC are as follows:

PBDTTT-EE: 0.32 g (87 %). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.8-6.9 (br, 3H), 4.5-3.8 (br, 6H), 1.9 (br, 3H), 1.8-1.3 (br, 24H), 1.2-0.8 (br, 18H). M_n = 41.9 K, M_w = 124.2 K, PDI = 2.97.

PBDTTT-ED: 0.33 g (80 %). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.9-6.8 (br, 3H), 4.6-3.7 (br, 6H), 1.9 (br, 4H), 1.8-1.1 (br, 34H), 1.2-0.85 (br, 15H). M_n = 20.0 K, M_w = 48.0 K, PDI = 2.40.

PBDTTT-DE: 0.35 g (82 %). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.8-6.8 (br, 3H), 4.6-4.0 (br, 6H), 1.9 (br, 5H), 1.8-1.1 (br, 44H), 1.05-0.85 (br, 12H). M_n = 41.3 K, M_w = 109.6 K, PDI = 2.66.

PBDTTT-DD: 0.44 g (94 %). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 7.8-6.9 (br, 3H), 4.6-3.8 (br, 6H), 1.9 (br, 6H), 1.8-1.2 (br, 54H), 1.2-0.85 (br, 9H). M_n = 18.0 K, M_w = 48.9 K, PDI = 2.70.

II. Differential Scanning Calorimetry (DSC) curves and heat capacity calculation

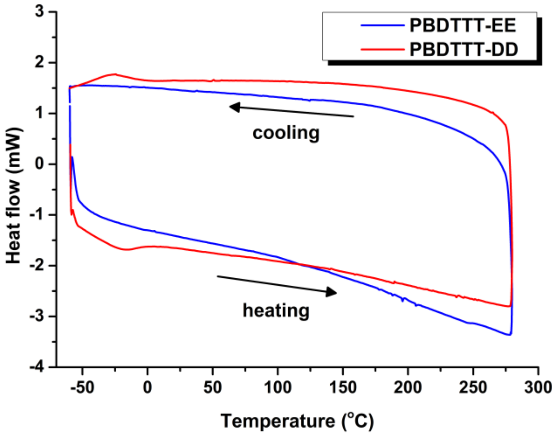

Figure S2. The heat flow changes as a function of temperature in DSC measurements.

The mass heat capacity can be calculated using the following relationship,

$$C_p = \frac{\Delta Y}{m\beta} \tag{1}$$

Where, ΔY is the heat flow found at given temperature, m is mass of the material being used in the DSC measurements, and β is the scan rate (degree sec^{-1}) used.

Near room temperature, $\Delta Y_{EE} = 1.45\text{mW}, \Delta Y_{DD} = 1.6\text{mW}$. The amount of material used in the scan: m=3.186 mg for PBDTTT-EE, m=3.3252 mg for PBDTTT-DD. The scanning rate has been set at 1/6 degree sec^{-1} (10 degree min^{-1}). Using the above values give Cp= 2.73 J g^{-1} K^{-1} for PBDTTT-EE polymer, and Cp= 2.887 J g^{-1} K^{-1} for PBDTTT-DD polymer.

III SAXS measurements

The SAXS experiments were conducted using a BrukerAXS NANAOSTAR equipped with a Cu source which emits X-ray at the wavelength of 1.54184 Å. HiStar 2D multiwire detector was used for data acquisition over the 2-theta (2θ) range: $0.3^{\circ} \leq 2\theta \leq 11.5^{\circ}$ with a sample-detector distance of 26.11 cm. Glassy carbon which was built-in from factory was employed to characterize sample transmission. The scattering signal of the glass substrate was subtracted. The collecting time of each sample was 1 hour under working voltage of 45 kV and current of 0.65 mA.

IV Modeling the effective thermal conductivity in polymer films using the effective medium theory

The effective medium theory we use to describe the effective thermal conductivity is a modified formulation for describing nanocomposites, where the inclusion size is smaller than the phonon mean free path (MFP)[1]. To apply this theory to our problem, the host phase is defined as the amorphous polymers (the majority) and the nanoparticles correspond to the crystalline polymer domains (the minority).

The task is divided into three steps:

1) Find out the effective thermal conductivity of the host phase
2) Find out the effective thermal conductivity of the nanoparticles
3) Calculate the effective thermal conductivity of the composite

First, we determine the host phase effective thermal conductivity. The thermal conductivity of a medium is related to its heat carrier MFP according to the following kinetic theory expression

$$k = \frac{1}{3} C \upsilon \Lambda \tag{2}$$

where C is the volumetric specific heat, v is the phonon group velocity, and Λ is the MFP. The effective MFP of the host phase is given by the following equation:[1]

$$\frac{1}{\Lambda_{eff,h}} = \frac{1}{\Lambda_{b,h}} + \frac{3\varphi}{2d} \tag{3}$$

where φ is the volume fraction of the nanoparticles (crystallinity of the polymer film), d is the diameter of the nanoparticle (crystallite size), and $\Lambda_{b,h}$ is the heat carrier MFP in the bulk host phase without any nanoparticles. The bulk host phase here refers to the amorphous matrix of the polymers. Because of the disorder scattering, the heat carrier MFP, $\Lambda_{b,h}$, is expected to be small. Since heat transfer through the covalent bonds are efficient, the heat carriers are not expected to be scattered much along the chain backbone and along the side chains. The limiting length for heat carrier transport is thus believed to be the characteristic length of the local order – the d-spacing. Hence, we set $\Lambda_{b,h}$ to be proportional to the d-spacing. It is found that the first term on the right hand side of Eq. (3) dominates, and the term $3\varphi/2d$ is about one magnitude smaller than the first term. Therefore the effective heat carrier MFP of the host phase can be represented by the d-spacing, d_h. In the following discussion, we use d_h to represent $\Lambda_{b,h}$ for convenience and drop the $3\varphi/2d$ term.

Second, we determine the thermal conductivity of the crystallite. Similarity, the effective thermal conductivity of the crystallites is related to the phonon MFP, which is described by the following formulation:

$$\frac{1}{\Lambda_{eff,p}} = \frac{1}{\Lambda_{b,p}} + \frac{1}{d} \tag{4}$$

In this case, contrary to the host phase, the phonon MFP of the perfect crystalline polymer, $\Lambda_{b,p}$ is much larger than the crystallite size. Therefore, the actual crystallite size, d_p, in the polymer, is taken as the effective phonon MFP, $\Lambda_{eff,p}$.

Third, we calculate the effective thermal conductivity of the composite. The equation for calculating the effective thermal conductivity of such a composite system was originally developed by Nan et al.[2] and further developed to take into account of the size effect in nanocomposites by Minnich et al. in ref [1]. It is written as,

$$k_{eff}(\Phi, d) = \frac{1}{3} C_h \upsilon_h \frac{1}{(1/\Lambda_h) + (\Phi/4)} \times \frac{k_p(d)\,(1 + 2\alpha(\Phi, d)) + 2k_h(\Phi) + 2(\Phi d/6)[k_p(d)\,(1 - \alpha(\Phi, d)) - k_h(\Phi)]}{k_p(d)\,(1 + 2\alpha(\Phi, d)) + 2k_h(\Phi) - (\Phi d/6)[k_p(d)\,(1 - \alpha(\Phi, d)) - k_h(\Phi)]} \tag{5}$$

where

$$\Phi = \frac{6\varphi}{d}$$

$$\alpha = \frac{2Rk_h}{d}$$

Here, k_h and k_p are the effective thermal conductivity of the amorphous phase and crystallite we have determined above. R is the thermal boundary resistance between the crystallites and the amorphous polymer matrix. The expression is reduced into a function of d_h, d_p, φ and R:

$$k_{eff} \propto d_h \bullet \frac{d_p(1 + 2\alpha) + d_h + 2 \bullet \varphi[d_p(1 - \alpha) - d_h]}{d_p(1 + 2\alpha) + d_h - \varphi[d_p(1 - \alpha) - d_h]} \tag{6}$$

where

$$\alpha = \frac{2}{d_p} R \cdot \frac{1}{3} C v d_h = \frac{2d_h}{d_p}\left(\frac{1}{3} C v R\right)$$

The values used in the above formula are summarized in the Table S1.

Table S1. Summary of parameters used in the effective medium approximation formula (6)

Polymer	d_p	d_h	φ
EE	4 nm	1.7 nm	0.066
ED	6 nm	3.1 nm	0.088
DE	6 nm	2.8 nm	0.2
DD	10 nm	3.3 nm	0.3

We assume that the specific heat and the heat carrier velocities are the same for all four polymers. A non-linear least squared fit allows us to determine the thermal boundary resistance term in the expression of α. We find

$$\frac{1}{3}CvR \approx 1$$

And the predicted effective thermal conductivities of four polymers using Eq. (5) are listed in the following table. We have also studied two other cases. In one case, we ignore the differences in d-spacing (composite effect only) and in the other case, we only consider the d-spacing effect while ignore the composite effect. These results are also listed in the Table S2.

Table S2. Summary of the predicted thermal conductivities from three different models

Polymer	composite effect only (W/mK)	d-spacing effect only (W/mK)	effective medium theory (W/mK)
EE	0.19	0.12	0.11
ED	0.2	0.22	0.21
DE	0.2	0.19	0.19
DD	0.25	0.23	0.24

V GISAXS measurements

Gazing incident small angle X-ray scattering (GISAXS) measurements were performed on the 12-ID-B beamline at the Advanced Photon Source of Argonne National Laboratory. The energy of the X-ray being used was 14 keV (λ=0.8856 Å). The GISAXS patterns were acquired at an incident angle of 0.1°, above the critical angle of PBDTTT while below the critical angle of the Si substrate. The line cut profiles were generated by GISAXSshop plugin (https://sites.google.com/site/byeongdu/software) in the IGORpro environment and fitted to gaussian functions to obtain d-spacing information.

VI AFM imaging of the π-π stacking in PBDTTT-DD polymer film

The PBDTTT-DD polymer was chosen for the study because of its high crystallinity feature. The polymer was spin-coated on a silicon wafer substrate (spin coating protocols is the same as described in the manuscript). The π-π stacking order of this type of polymer has a orientation preferrence parallel to the substrate according to previous GIWAXS studies.[3, 4] In our work, we performed AFM imaging on the polymer surface (tapping mode) and resolved the π-π stacking distance by measuring the height difference between crystalline polymer grains that have few lamellae layers differences.

In figure S3, two height image of polymer surface (50 nm x50 nm) was shown. Ordered nano crystallites were found in those images, and the height difference between them are about 1~2 stacking layers. The average π-π stacking distance was about 3.7-3.9 Å in DD polymer, which is in good agreement with that found in a PTB polymer modified with linear side chains of similar length (PTB1, 3.65 Å).[4]

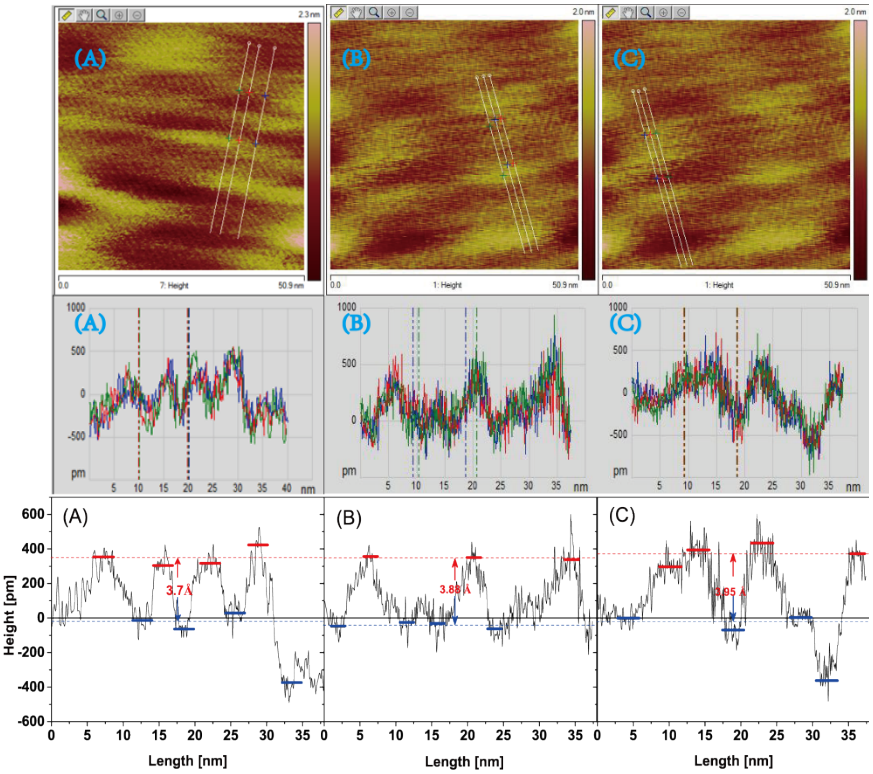

Figure S3. π-π stacking distance in PBDTTT-DD polymer film measured from AFM height images. First row: AFM height images of the sample surface with crystalline domains (B and C are the same image), 50 nm x 50 nm in size, and color scale bar represents height range from 0 to 2 nm. Section lines cuts are indicated in the images. Second row: overlapped height profiles from three section line cuts. Third row: averaged height profiles at three sample positions. π-π stacking distances are estimated from the peak-to-valley height difference.

References:

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