Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Structural Control of Charge Transport in Polymer Monolayer Transistors by a Thermodynamically Assisted Dip-Coating Strategy

Chenming Ding[a,b], Junyang Deng[a], Miao Cheng[a], Mengmeng Li[a,b], Ling Li[a]*

[a]Key Laboratory of Microelectronic Devices and Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, 100029 Beijing, China

[b]University of Chinese Academy of Sciences, 100049 Beijing, China.

*Email: limengmeng@ime.ac.cn

Supplementary note 1：

The maximum rate of overall crystallization as a function of temperature is defined by

$$\frac{d}{dT}(Ju^n)\Big|_{T=T_{max}^{(overall)}} = 0$$

where T is temperature, *J* is the function of nucleation rate at various T (Eq. S1), *u* is the function of growth rate at various T (Eq. S4), *n* is the number of independent directions of growth. In this work, n is taken as 3. The overall crystallization rate is determined by the point where the slope of f(T) = Ju^n is 0. That is, the overall crystallization rate is determined by f(T) = Ju^n.

J can be written as:

$$J = A \cdot D\exp\left(-\frac{\frac{16\pi\alpha^3\Phi}{3}\left(\frac{q}{k_B T_m}\right)}{\frac{T}{T_m}\left(1-\frac{T}{T_m}\right)^2}\right) \quad \text{(S1)}$$

where the A is constant, D the effective diffusion coefficient governing the processes of aggregation of ambient phase particles to crystal clusters, T_m the equilibrium melting (or liquidus) temperature, for PffBT4T-2DT is 533K[S1], α is found to have value commonly in the range 0.3 < α < 0.6[S2] (in this work α is taken as 0.3), k_B the Boltzmann constant and q is the latent heat of crystallization per particle. Φ is the nucleation activity factor, where Φ = 1 indicates homogeneous and Φ < 1 heterogeneous nucleation. In this work Φ is taken as 0.032.

D can be written as:

$$D = D_0\exp\left(-\frac{E_D}{k_B T}\right) \quad \text{(S2)}$$

where the E_D is the activation energy for diffusion, and the value of 1.6 x 10^{-19} J [S3] is used.

q can be written as:

$$q = T_m \Delta S_m \quad \text{(S3)}$$

where ΔS_m is the melting entropy per particle at the equilibrium melting (or liquidus) temperature T_m, for PffBT4T-2DT is 22 J g^{-1} [S1] = 4.24 x 10^{-18} J/ particle = 8 x 10^{-21} J/ (K particle), M_n = 116.4 kg mol^{-1}.

u can be written as:

$$u = B \cdot D\left[1-\exp\left(\frac{\Delta\mu}{k_B T}\right)\right] \quad \text{(S4)}$$

where the B is constant, $\Delta\mu$ is the thermodynamic driving force that can be written:

$$\Delta\mu = q\left(1 - \frac{T}{T_m}\right) \quad \text{(S5)}$$

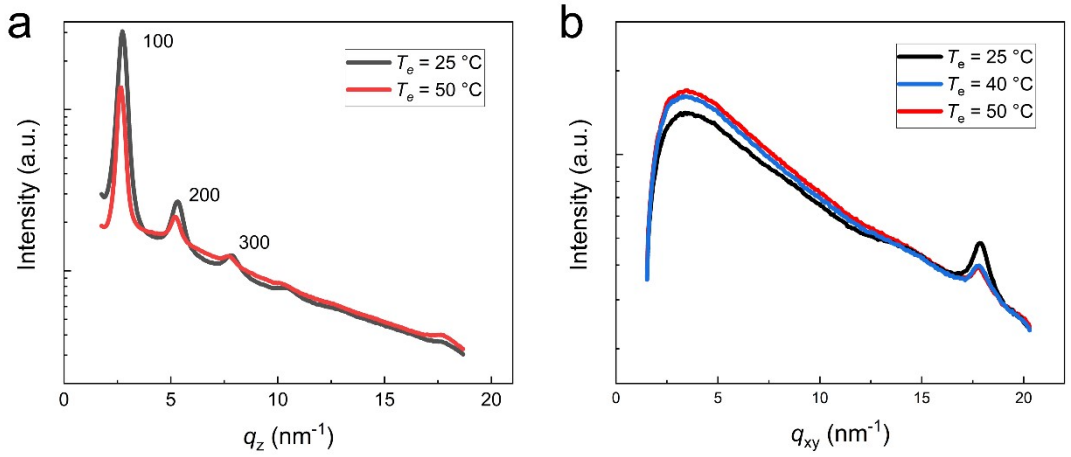

Fig. S1 a) 1D GIWAXS out-of-plane profiles of PffBT4T-2DT thin films coated at T_e = 25 and 50 °C. b) 1D GIWAXS in-plane profiles of PffBT4T-2DT thin films coated at T_e = 25, 40 and 50 °C.

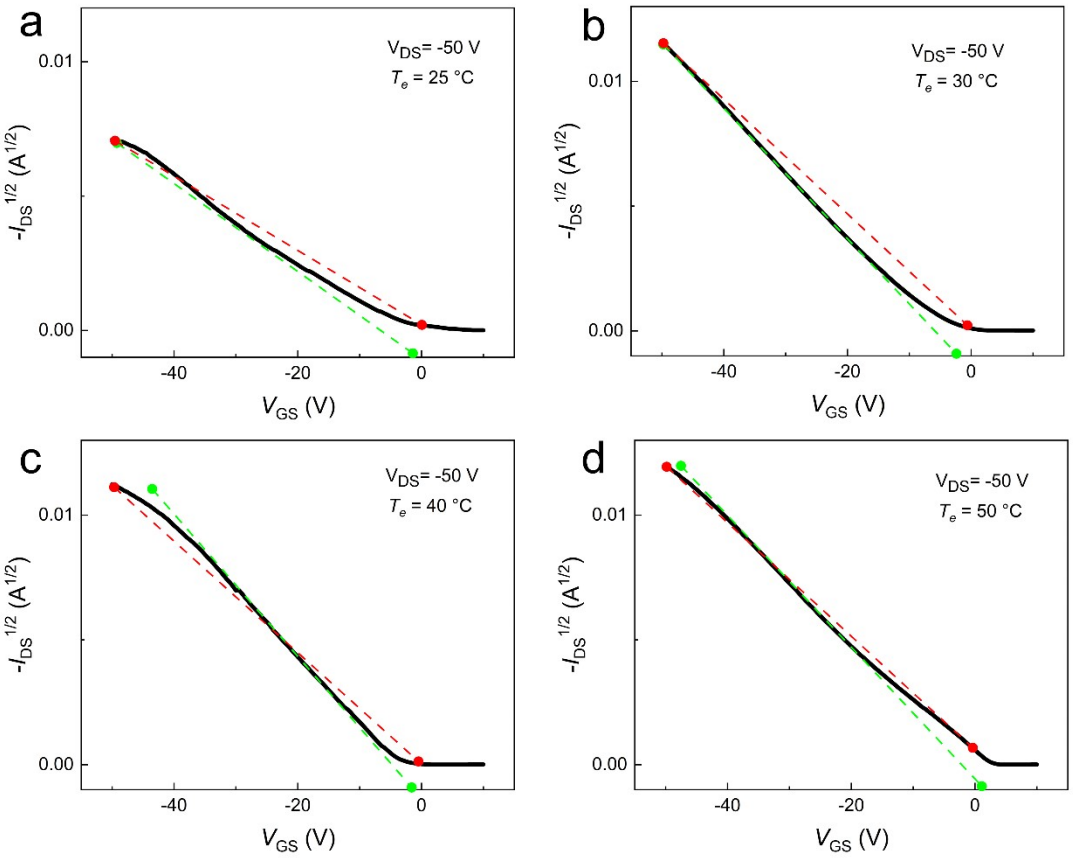

Fig. S2 a)–d) The extraction process of reliability factor γ for L=10 μm monolayer FETs with different T_e.

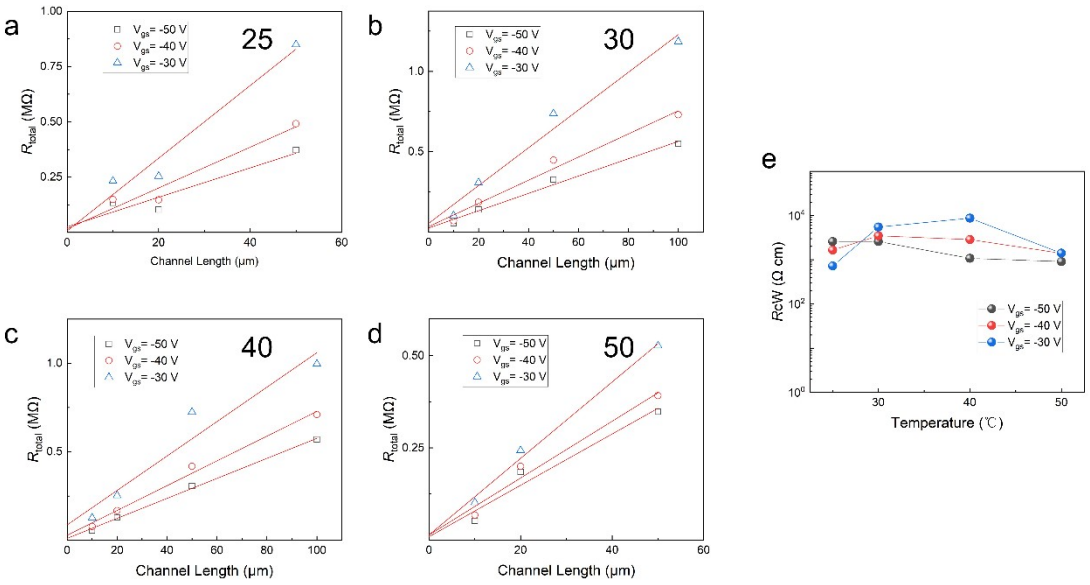

Fig. S3 a)–d) Total device resistance (R_{total}) as a function of the channel length (L) with various V_{GS} for PffBT4T-2DT monolayer FETs at different T_e. The channel width is 2000 μm. e) Contact resistance times channel width (W) as a function of T_e.

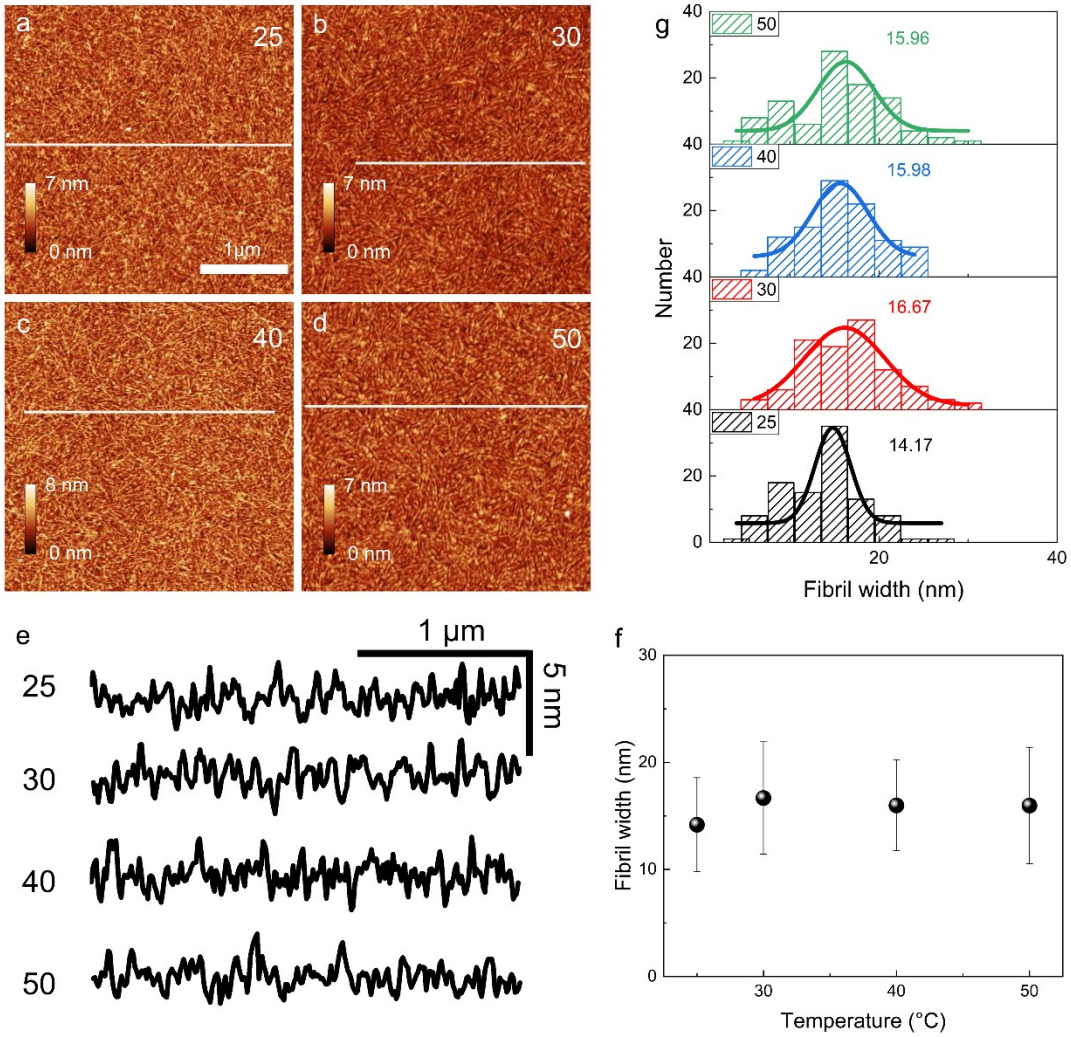

Fig. S4 a)–d) AFM height images of PffBT4T-2DT monolayers on the source-drain electrode dip-coated with different T_es. e) Corresponding height profiles of the white lines in (a)–(d). f) Fibril width as a function of T_e. The average values and standard deviation for each sample are analyzed from over 100 fibrils. g) Distributions of the fibril width extracted from the AFM height images.

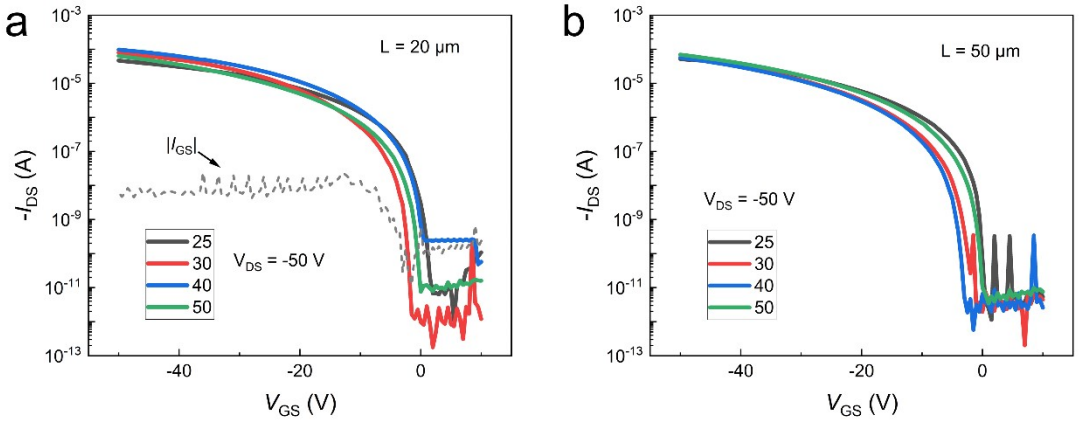

Fig. S5 a) Transfer characteristics of PffBT4T-2DT monolayer FETs with a) L=20 μm and b) L=50 μm) at various T_es (25, 30, 40, and 50 °C). The dash line in (a) indicates the gate leakage current (I_{GS}).

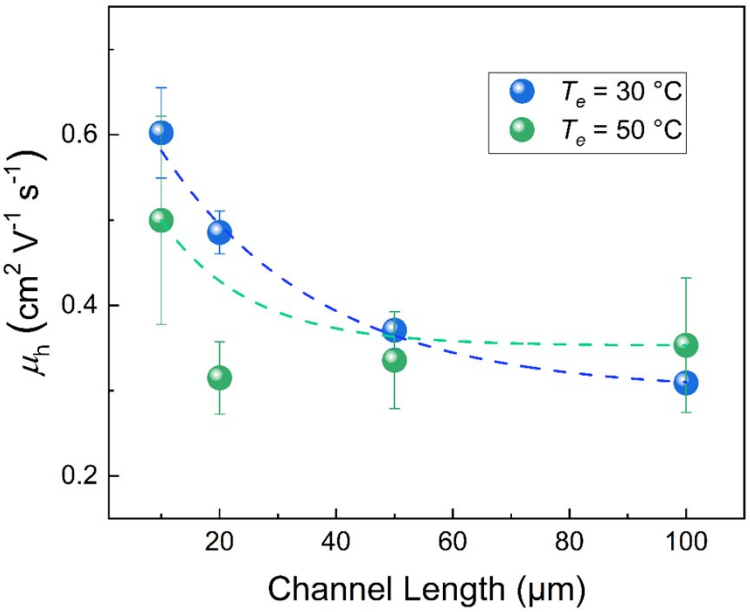

Fig. S6 Saturated field-effect mobility (μ_h) of polymer monolayer FETs as a function of channel length, where different T_es (30 and 50 °C) are applied.

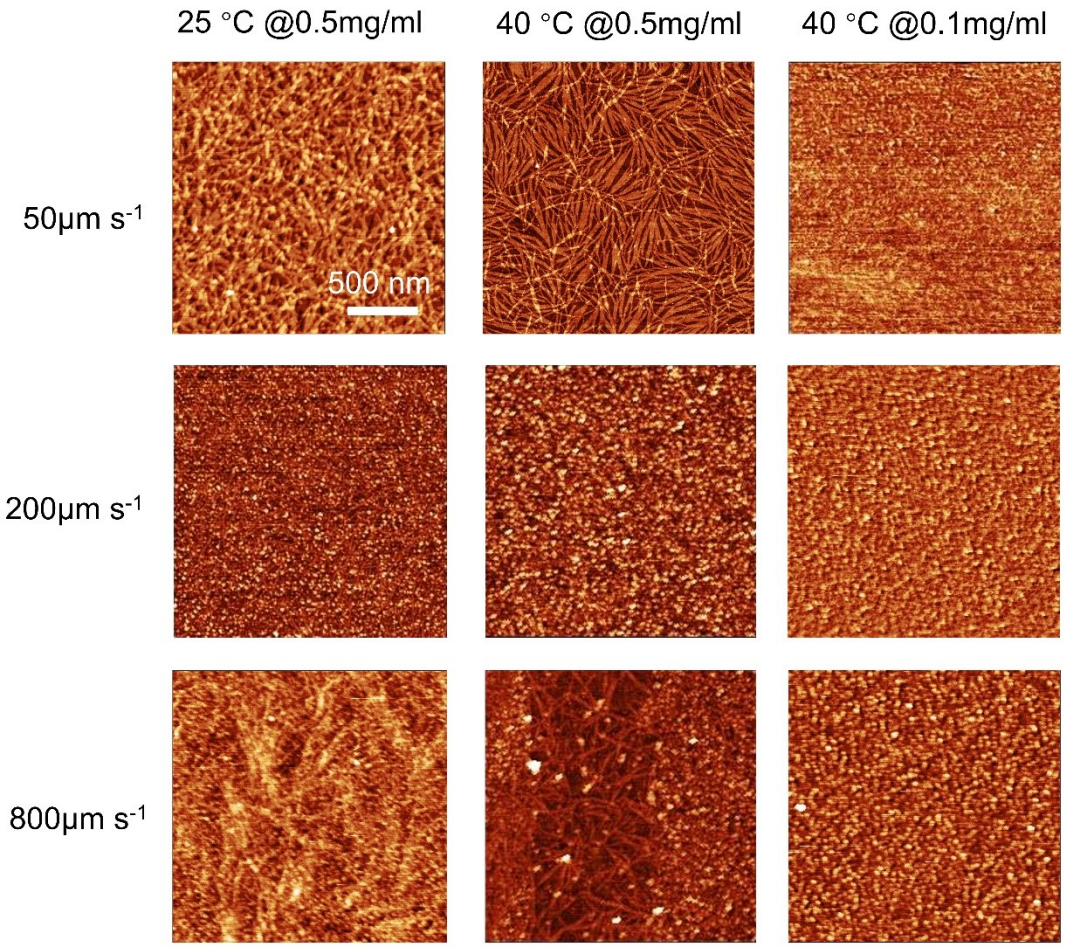

Fig. S7 AFM height images of PffBT4T-2DT ultrathin films fabricated under different conditions.

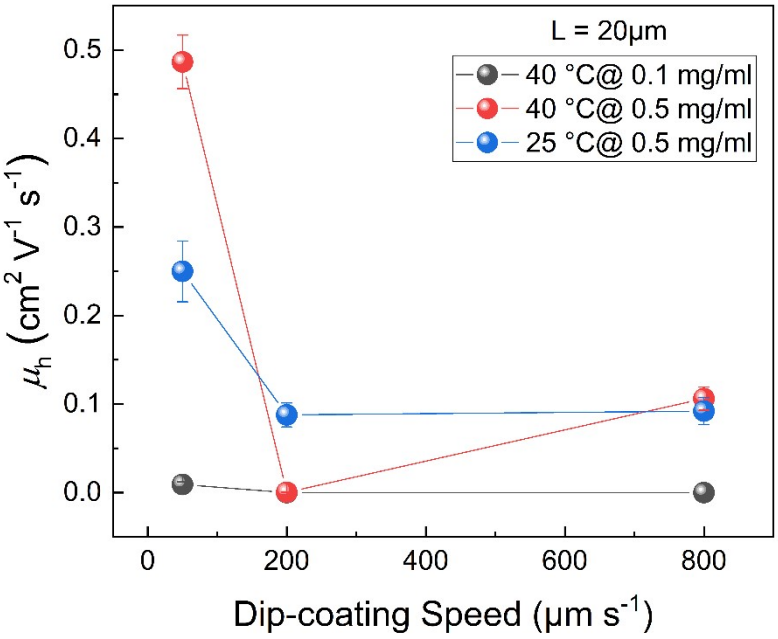

Fig. S8 Mobility as a function of the dip-coating speed under various conditions.

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