Microstructure engineering of polymer semiconductor thin films for high-performance field-effect transistors using a bi-component processing solution

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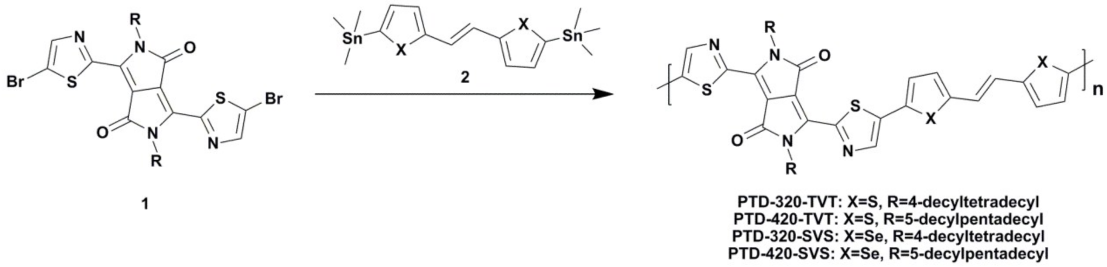


Scheme S1 Synthetic route of TZDPP-based polymers of **PTD-320-TVT, PTD-420-TVT, PTD-320-SVS, PTD-420-SVS**. Regents and conditions: $Pd_2(dba)_3$, P(o-tol)$_3$, toluene, 110°C.

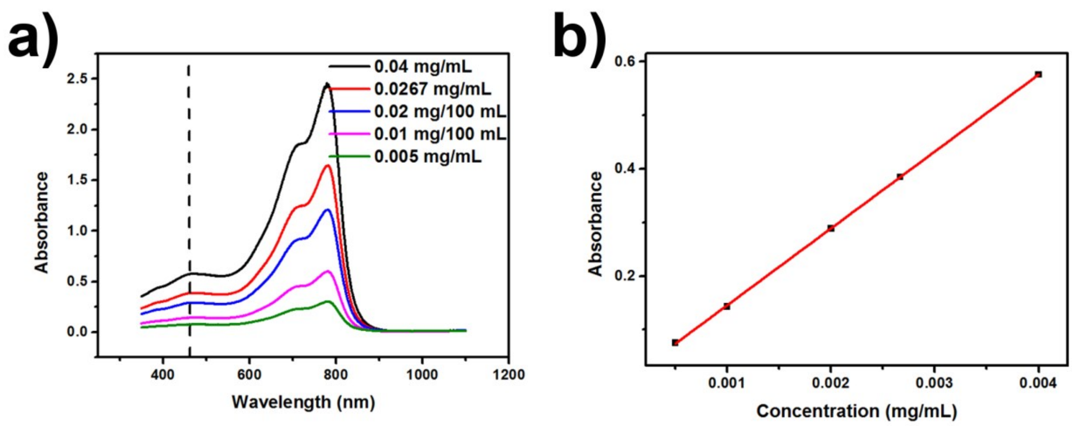


Fig. S1 a) UV-vis absorption spectra of the **PTD-10-TVT** in DCB with different concentration; b) the concentration fitted against their absorbance.

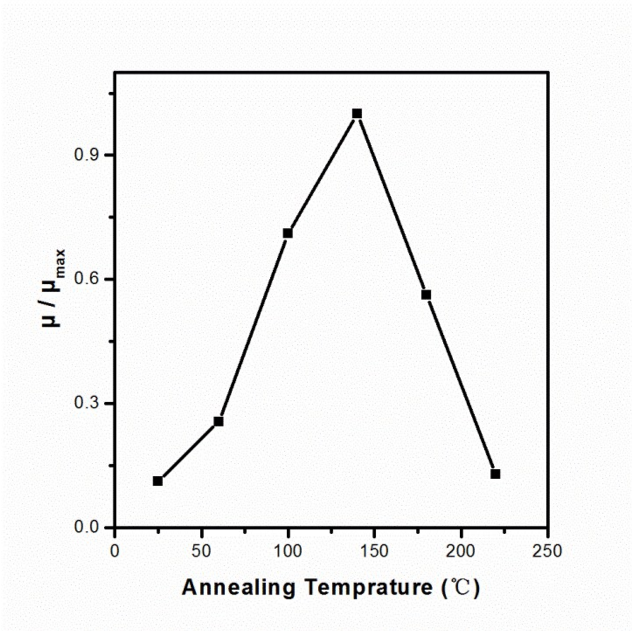


Fig. S2 Mobilities (p-type) under different annealing temperature for **PTD-10-TVT** (annealing time: 9 min).

Table S1 Parameters of the FET devices and polymer PTD-10-TVT thin films processed with DCB or DCB:CF (5:1) under different annealing time at the temperature of 140 ºC

Processing solvent	Annealing time (min)	Mobility (cm^2 V^{-1} s^{-1})	correlation lengths (Å)	Paracrystalline Distortion Parameters g (%)
DCB	As cast	0.21	121.32	8.60
	1	0.26	127.94	8.53
	3	0.29	131.12	7.93
	5	0.32	134.18	7.10
	7	0.28	136.20	7.45
	9	0.31	130.31	7.63
DCB:CF (5:1)	As cast	0.55	149.36	7.19
	1	0.61	150.42	7.28
	3	1.06	161.14	6.37
	5	1.28	157.54	5.41
	7	0.92	158.32	5.83
	9	0.95	160.73	5.36

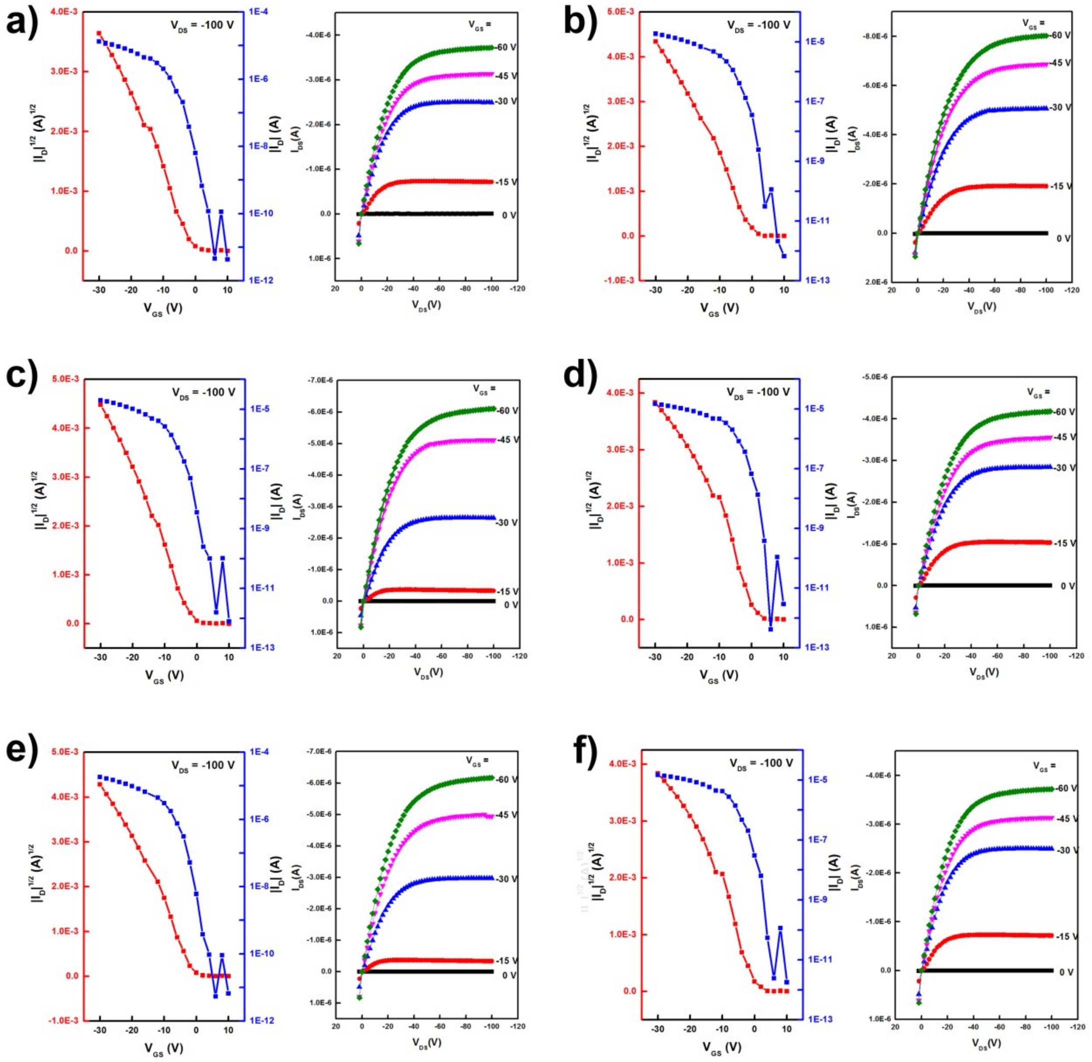


Fig. S3 Transfer and output curves of the **PTD-10-TVT** FET devices fabricated from the DCB with the annealing time of a) as cast; b) 1 min; c) 3 min; d) 5 min; e) 7 min; f) 9 min at the annealing temperature of 140 ^{o}C.

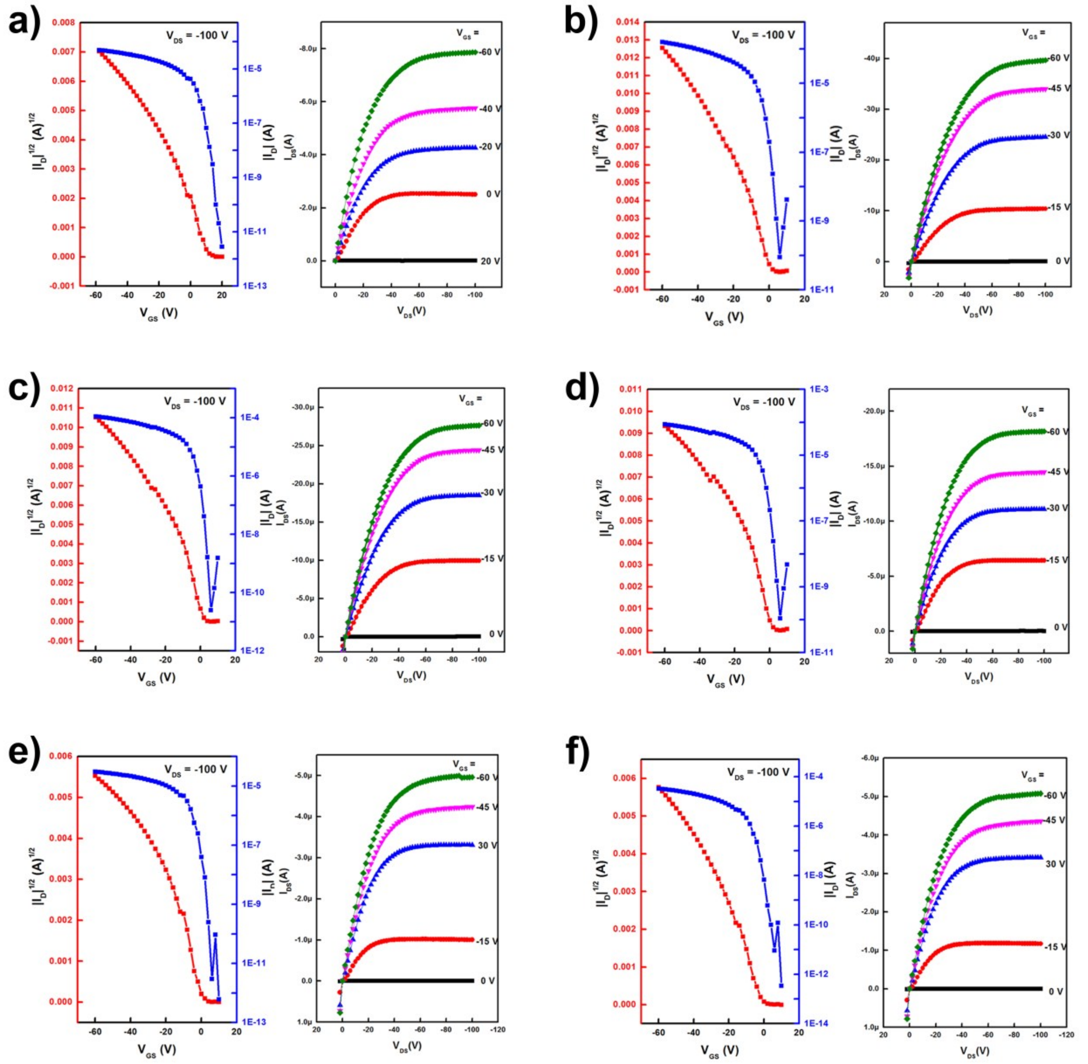


Fig. S4 Transfer and output curves of the **PTD-10-TVT** FET devices fabricated from the bi-component solvent with the ratio of DCB:CF= a) pure DCB; b) 6:1; c) 5:1; d) 4:1; e) 3:1; f) 2:1 at the annealing temperature of 140 ºC with the annealing time of 5 min.

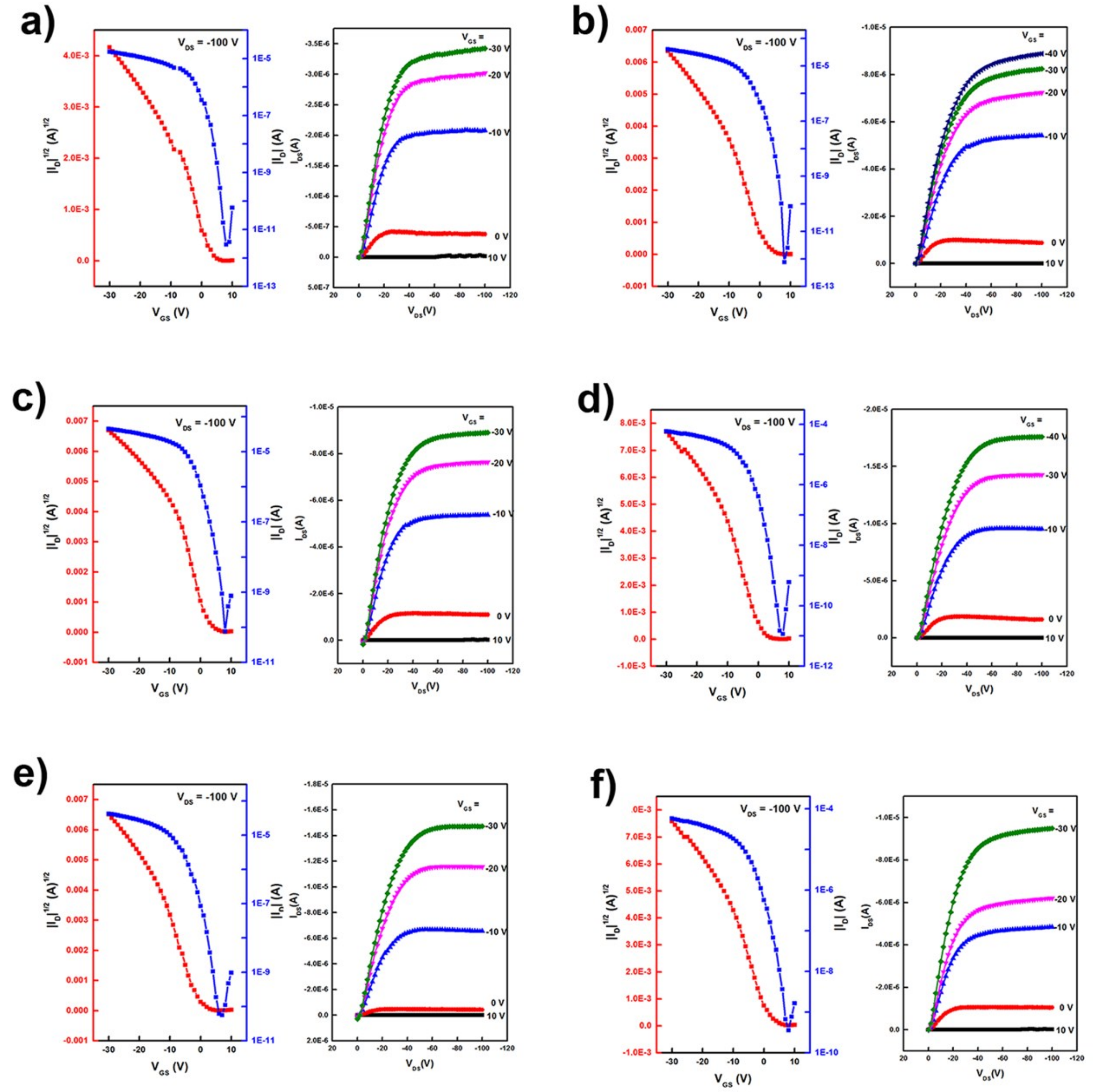


Fig. S5 Transfer and output curves of the **PTD-10-TVT** FETs fabricated from the bi-component solvent of DCB:CF (5:1) with the annealing time of a) as cast; b) 1 min; c) 3 min; d) 5 min; e) 7 min; f) 9 min at the annealing temperature of 140 ºC.

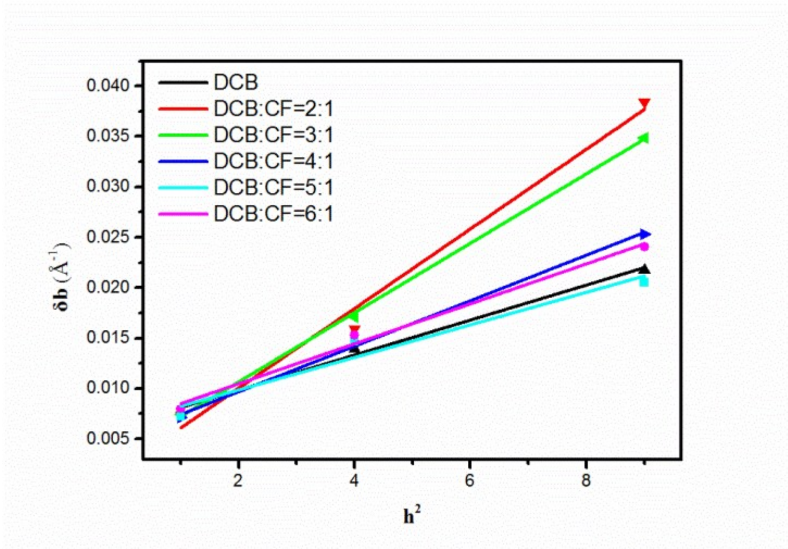


Fig. S6 δ b–h^2 curves of the annealed films for **PTD-10-TVT** processed with different bi-component solvents. The parameters were extracted from GIXRD analysis, and the values of the corresponding fitting linear were listed in **Table S2**.

Table S2 Values of the corresponding fitting linear of the PTD-10-TVT-films processed with different processing solvent

Ratio(DCB:CF)	Integral Breadth (Å^{-1})			R^2	a	b	g
	100	200	300				
DCB	0.00576	0.0159	0.0258	0.993	0.0019	0.0064	0.0653
6:1	0.00797	0.0153	0.0240	0.988	0.0020	0.0065	0.0666
5:1	0.00724	0.01472	0.0206	0.997	0.0016	0.0066	0.0597
4:1	0.00718	0.0146	0.0253	0.998	0.0023	0.0052	0.0716
3:1	0.00750	0.0171	0.0349	0.999	0.0034	0.0038	0.0874
2:1	0.00737	0.0159	0.0385	0.988	0.0039	0.0022	0.0935

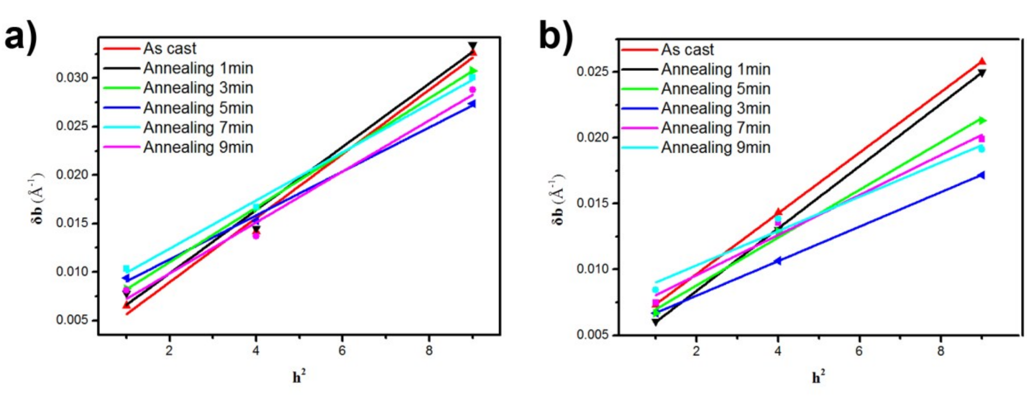


Fig. S7 δ b–h^2 curves of the annealed films for **PTD-10-TVT** processed with a) DCB and b) DCB:CF (5:1). The parameters were extracted from GIXRD analysis.

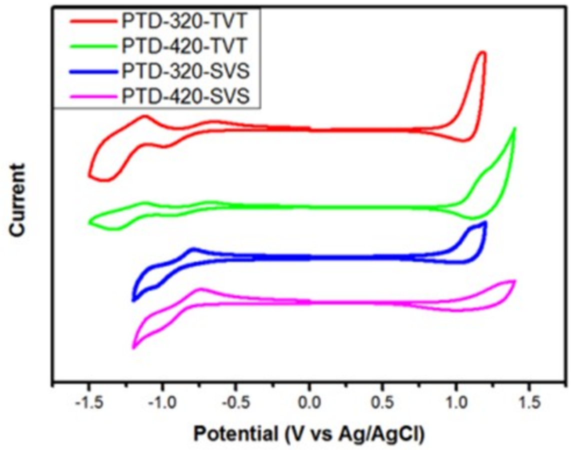
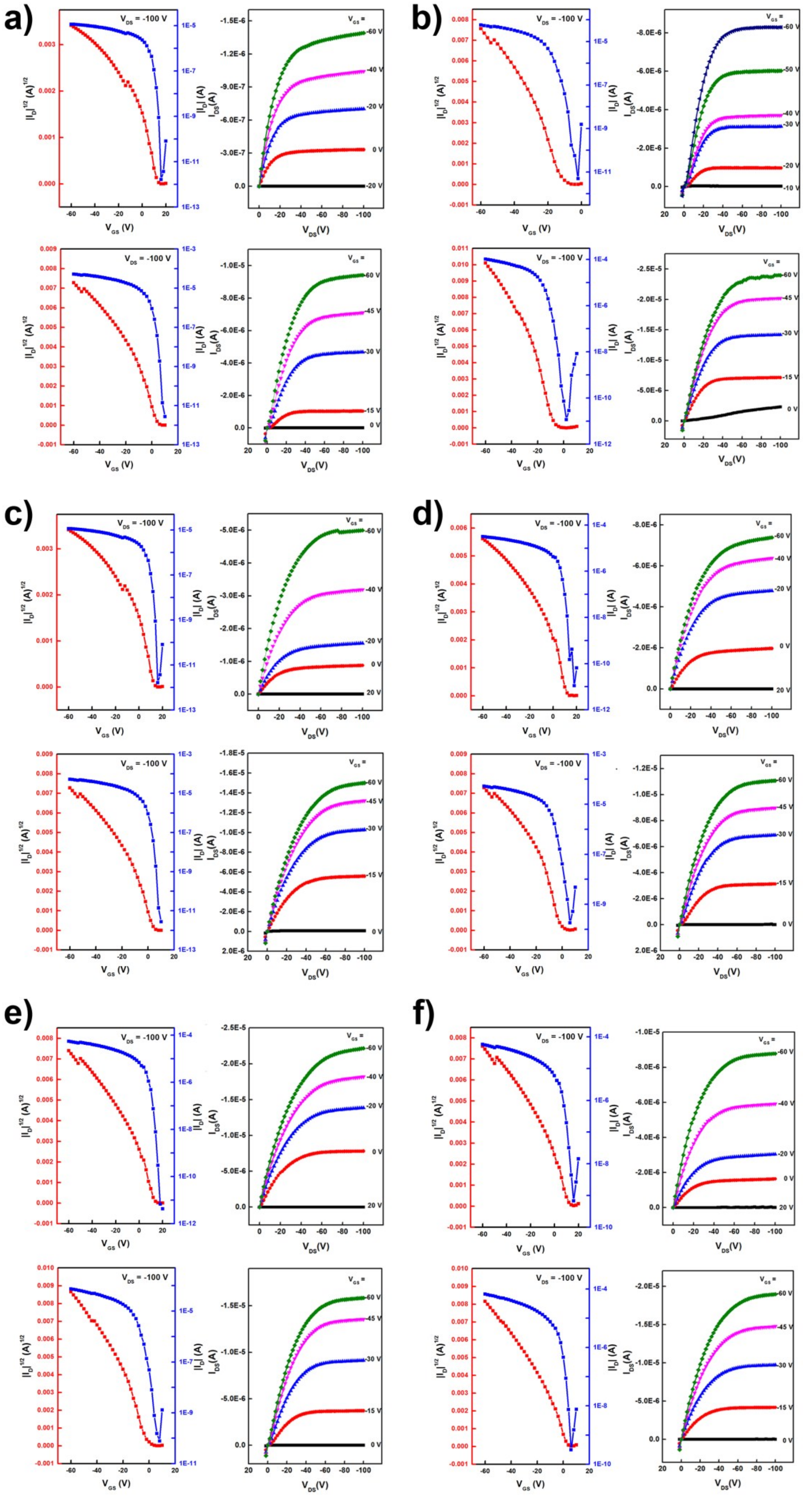


Fig. S8 Cyclic voltammetry curves of **PTD-320-TVT; PTD-420-TVT; PTD-320-SVS; PTD-420-SVS**. The chemical structures can be found in Fig. 1.



a)
b)
c)
d)
e)
f)
V_DS = -100 V
V_GS =
|I_D|^1/2 (A)^1/2
|I_D| (A)
I_DS(A)
V_GS (V)
V_DS(V)
-60 V
-40 V
-20 V
0 V
20 V
-50 V
-30 V
-10 V
-45 V
-15 V

Fig. S9 Transfer (left) and output (right) curves of BGBC FET devices based on a) **PTD-8-TVT**; b) **PTD-320-TVT**; c) **PTD-8-SVS**; d) **PTD-10-SVS** e) **PTD-320-SVS**; f) **PTD-420-SVS** fabricated with DCB (top) and the bi-component solvent (bottom) of DCB:CF=(5:1) at the annealing temperature of 140 ºC with the annealing time of 5 min.

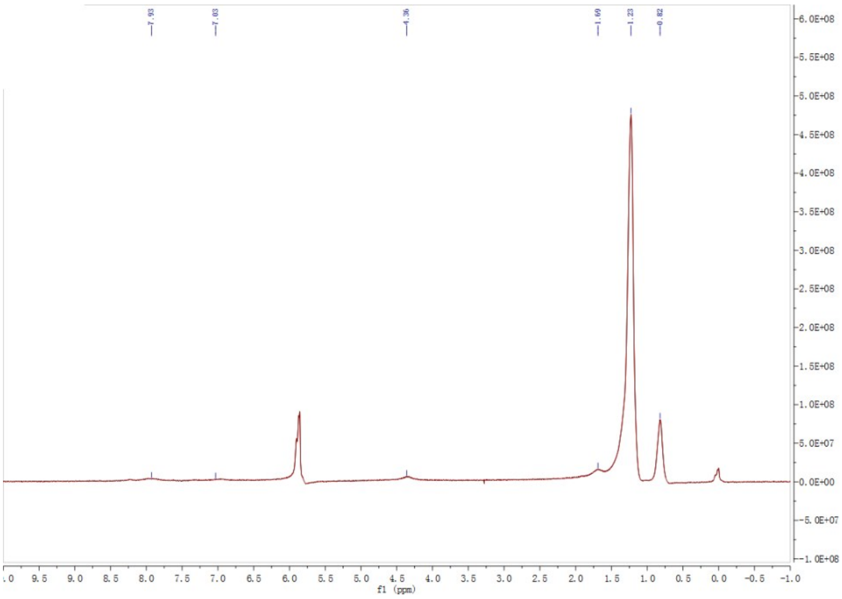
Supplementary Note S1

The details of multiple-peak fitting, minor polarization correction could be found in previous reports. (a) M. R. Hammond, R. J. Kline, A. A. Herzing, L. J. Richter, D. S. Germack, H.-W. Ro, C. L. Soles, D. A. Fischer, T. Xu, L. Yu, M. F. Toney and D. M. DeLongchamp, ACS Nano, 2011, 5, 8248; (b) X. Zhang, H. Bronstein, A. J. Kronemeijer, J. Smith, Y. Kim, R. J. Kline, L. J. Richter, T. D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch and D. M. DeLongchamp, Nat. Commun. 2013, 4, 2238; (c) J. L. Baker, L. H. Jimison, S. Mannsfeld, S. Volkman, S. Yin, V. Subramanian, A. Salleo, A. P. Alivisatos and M. F. Toney, Langmuir 2010, 26, 9146.)

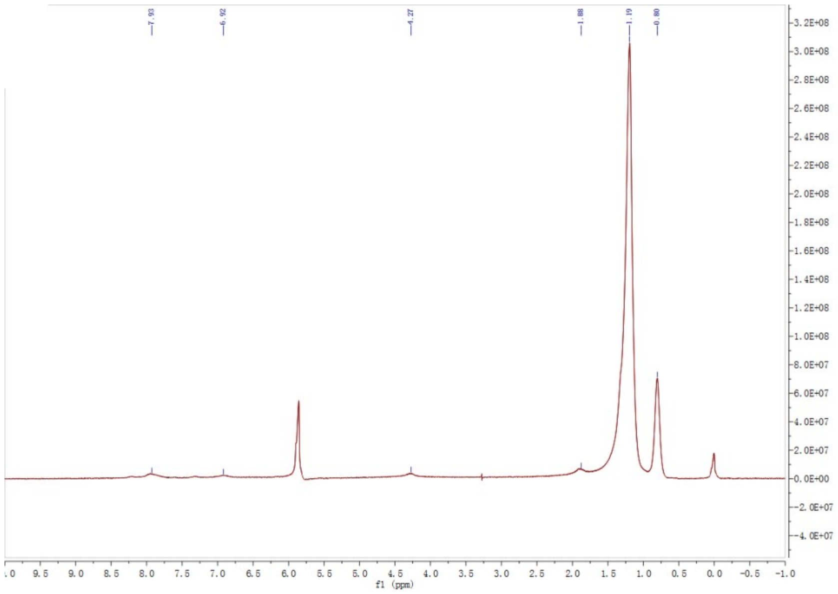
The 200 intensities were multiplied by sin ω to give a reasonable account of the population of crystallites with a given orientation. Then the second moment of the orientation distribution can be calculated by the following equation:

$$\langle \cos^2 \omega \rangle = \frac{\int_0^{90} I(\omega)(\cos^2 \omega)(\sin \omega)d\omega}{\int_0^{90} I(\omega)(\sin \omega)d\omega}$$

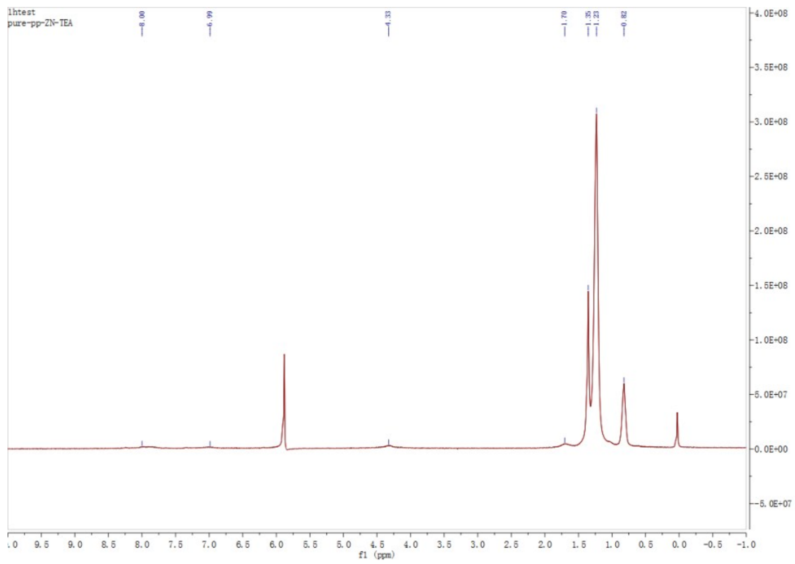
While I is the deconvoluted 200 intensity before sin ω correction



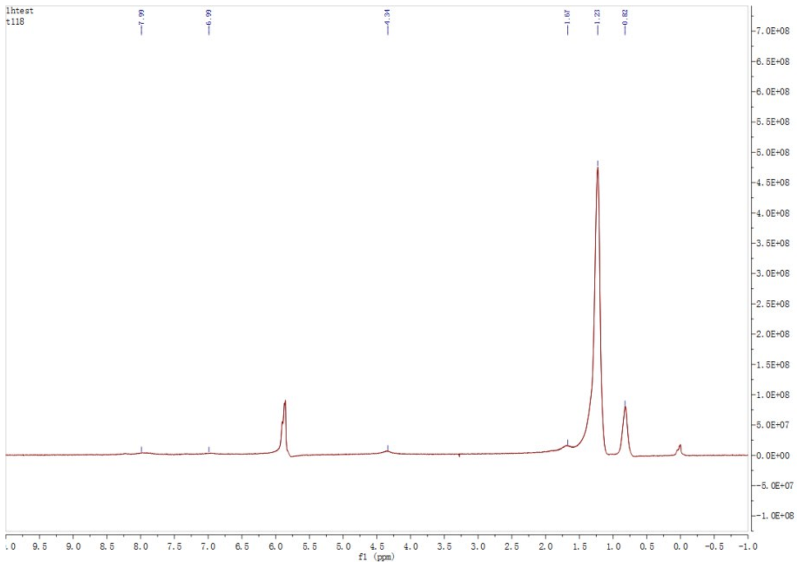
¹HNMR spectra of PTD-320-TVT



¹HNMR spectra of PTD-420-TVT



¹HNMR spectra of PTD-320-SVS



¹HNMR spectra of PTD-420-SVS