Supporting Information

Eutectic Friction Transfer Lithography: A Facile Solid-State Route for Highly Crystalline Semiconducting Polymers

Sangwon Eom,[a] Jae Hyun Sim,[a,b] Jongchan Kim,[a] Ngoc Bao Tran,[a] Myung Mo Sung,[a] Youngjong Kang*[a,c,d]

[a] Department of Chemistry, Hanyang University, Seoul, 04763, Korea
[b] Research Institute for Convergence of Basic Science
[c] Institute of Nano Science and Technology, Hanyang University, Seoul, 04763, Korea
[d] Research Institute for Natural Sciences, Hanyang University, Seoul, 04763, Korea
e-mail: youngjkang@hanyang.ac.kr

Experimental

Materials

Poly[4-(4,4-dihexadecyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-alt-[1,2,5]thiadiazolo[3,4-c]pyridine] (PCDTPT, > 99%, M_w = 76,000, 1-Material Inc.), poly(3-hexylthiophene-2,5-diyl) (P3HT, M_w = 70,000, Rieke Metals Inc.), poly[(5-fluoro-2,1,3-benzothiadiazole-4,7-diyl)(4,4-dihexadecyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)(6-fluoro-2,1,3-benzothiadiazole-4,7-diyl)(4,4-dihexadecyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene-2,6-diyl)] (PFT-100, M_w > 50,000, 1-Material Inc.), poly(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT, M_n ≤ 25,000, Sigma Aldrich Inc.), 1,3,5-trichlorobenzene (1,3,5-TCB, 99%, Sigma Aldrich Inc.), 1,4-dibromotetrafluorobenzene (1,4-DBTFB, ≥ 99%, Sigma Aldrich Inc.), naphthalene (99%, Sigma Aldrich Inc.), benzoic

acid (≥ 99.5%, Sigma Aldrich Inc.), poly(4-vinylphenol) ($M_n \leq 25{,}000$, Sigma Aldrich Inc.), polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning.), trichloro(octadecyl)silane (OTS, ≥ 90%, Sigma Aldrich Inc.).

Fabrication of Eutectic film by Eutectic Friction Method

Fabrication of eutectic pellet: Firstly, semiconducting polymer (P3HT, PCDTPT and F8BT) and volatile solid matrix (benzoic acid, 1,3,5-TCB, 1,4-DBTFB, and naphthalene) were mixed together in a weight ratio of 1:30, then it was dissolved in chloroform, and which was filtered through a syringe filter (PTFE, 0.2 μm pore) to remove dust and insoluble materials. The filtrate was dried at room temperature for 4 hr. After drying, the powder was ground again, and compressed with a pressure of ~600 MPa to make pellet (diameter = 1.2 cm, thickness = 5000 μm).

Fabrication of PDMS mold: Sylgard 184 and curing agent were mixed vigorously in a weight ratio of 10:1, and then gently poured it on a silicon wafer master mold. After heating at 80 ºC for 1 hr, PDMS mold was detached from the master mold.

Fabrication of EFT polymer films: Eutectic pellet was rubbed (friction transfer) on the pre-heated PDMS (50 °C) with a speed of 6000 mm/min with applying ~0.1 MPa. The pattern was transferred from PDMS mold onto the Si substrate by utilizing liquid-bridge-mediated transfer technique (LB-nTM). Ethanol was dropped on the pre-heated Si wafer at 60 °C, and then the PDMS mold was carefully placed on it. In this case, the attractive capillary force gradually increases as ethanol evaporated, and which pulls down the semiconducting wires onto the substrate.

Device fabrication

Bottom gate and top electrode structure devices were fabricated. Silicon substrate was cleaned by acetone, DI-water, and IPA in the sonicator for 15 min. After cleaning, substrate was kept in 100 ºC oven for 10 min to evaporate residue solvent. Then UVO cleaned for 15 min. Cleaned substrate was immersed in hexane (50 ml) + OTS (10 mmol) for 50 min for OTS treatment. The residual OTS was cleaned with hexane and subsequently purged with N2 gas. The semiconducting polymer microwires were transferred on to the substrate by using LB-nTM. Finally, 100 nm gold electrode is evaporated by thermal evaporator (Kim's Vacuum).

Characterizations

Optical microscope images and polarized optical microscope images were recorded on Olympus BX51 TR-N33MU. Scanning electron microscope images were recorded on Hitachi S-4800. UV-Vis absorptions and polarized UV-Vis absorptions were measured by Agilent Technologies 8453 UV spectrophotometer equipped with polarizers (Edmund Optics). Photoluminescence spectrums were measured by Perkin Elmer LS 55 fluorescence spectrometers. Grazing incidence X-ray diffraction data were measured on SmartLab (Rigaku) high resolution X-ray diffractometer. Electrical properties were measured on a probe station (MS TECH) equipped with a Keithley 4200A-SCS parameter analyzer. The field effect mobilities were extracted from saturation regime (V_{DS} = –70 V and V_{DS} = –80 V) by using $I_{DS} = Ci(W/2L)\mu(V_{GS}-V_{th})^2$ equation, where Ci is the gate dielectric layer capacitance per unit area, W/L is the channel width/length and V_{GS}, V_{th} are the gate voltage and threshold voltage.

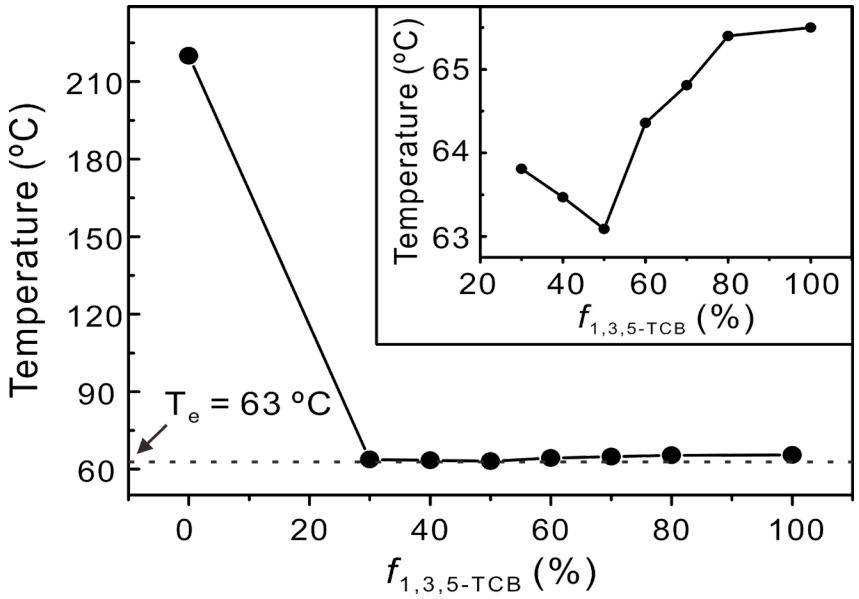

Figure S1. The change of melting point for the mixture of P3HT and 1,3,5-TCB as a function of the weight fraction of a matrix (f_x). Melting temperatures were determined by using DSC. Eutectic melting temperature was denoted by T_e.

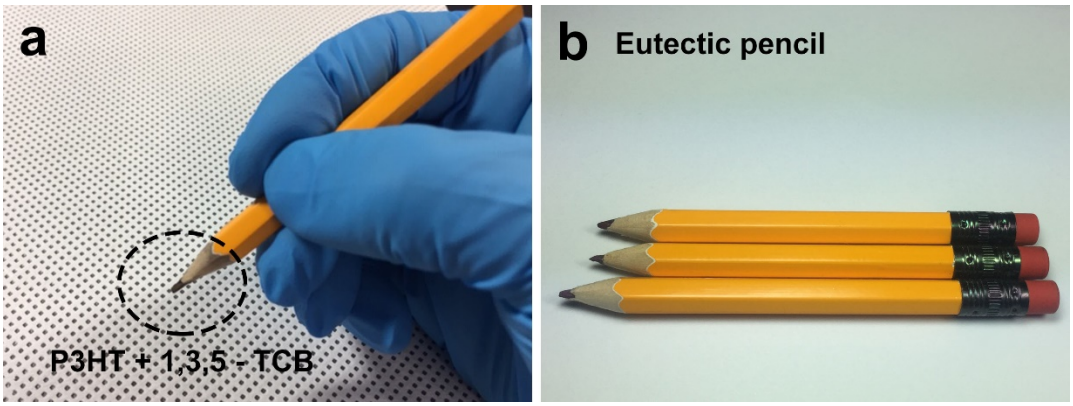

Figure S2. (a,b) The images of eutectic pencils. Eutectic pellet was inserted as a lead after trimming.

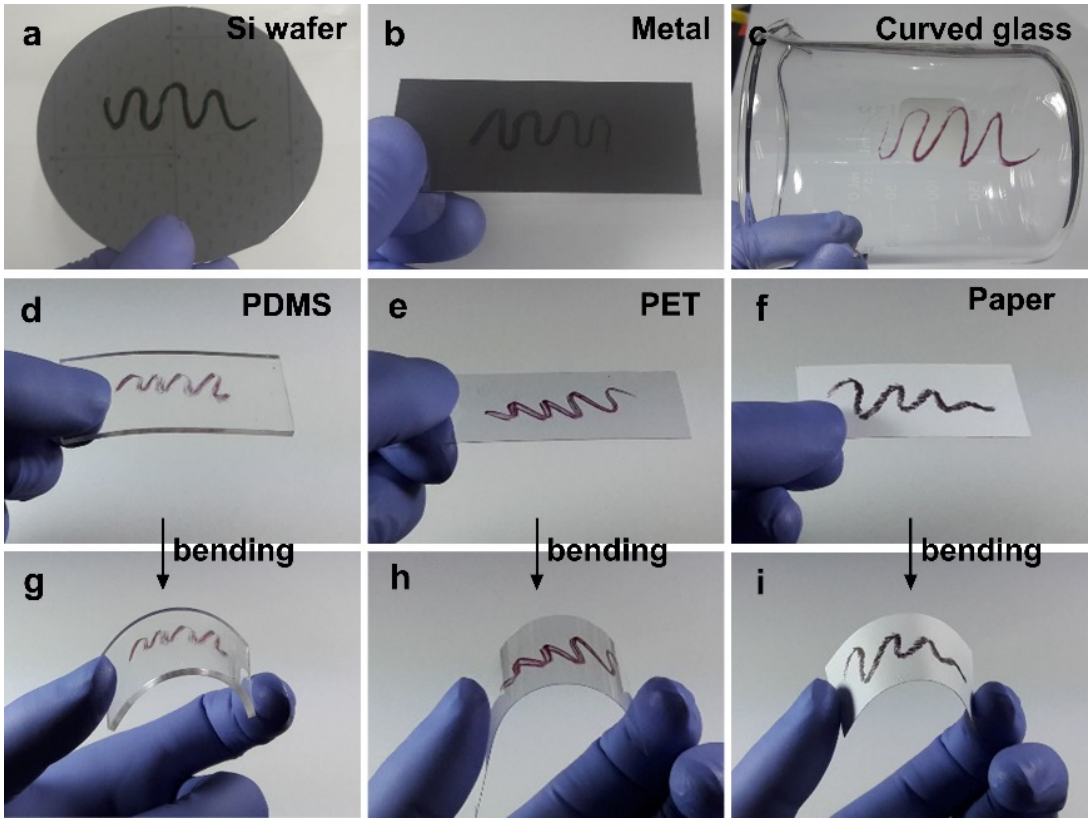

Figure S3. EFT films on various substrates including (a) silicon wafer, (b) metal (STS 304), (c) curved glass, (d) PDMS, (e) PET and (f) paper.

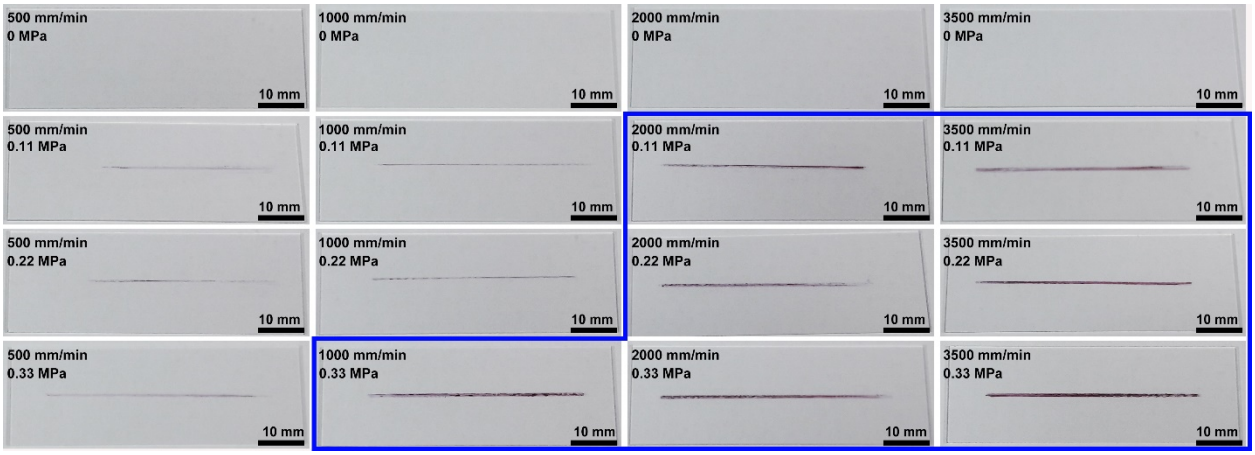

Figure S4. Optimization of the drawing speed and pressure of EFT process. The line pattern was drawn on the glass substrate with varying the speed and the compression pressure at the room temperature. The pen was perpendicular to the substrate. Generally, more uniform and dense line pattern was obtained as increasing the drawing speed. For our sample set done, the optimal condition was the drawing speed = 3500 mm/min under 0.2-0.3 MPa of compression. The optimum condition was highlighted with the blue box.

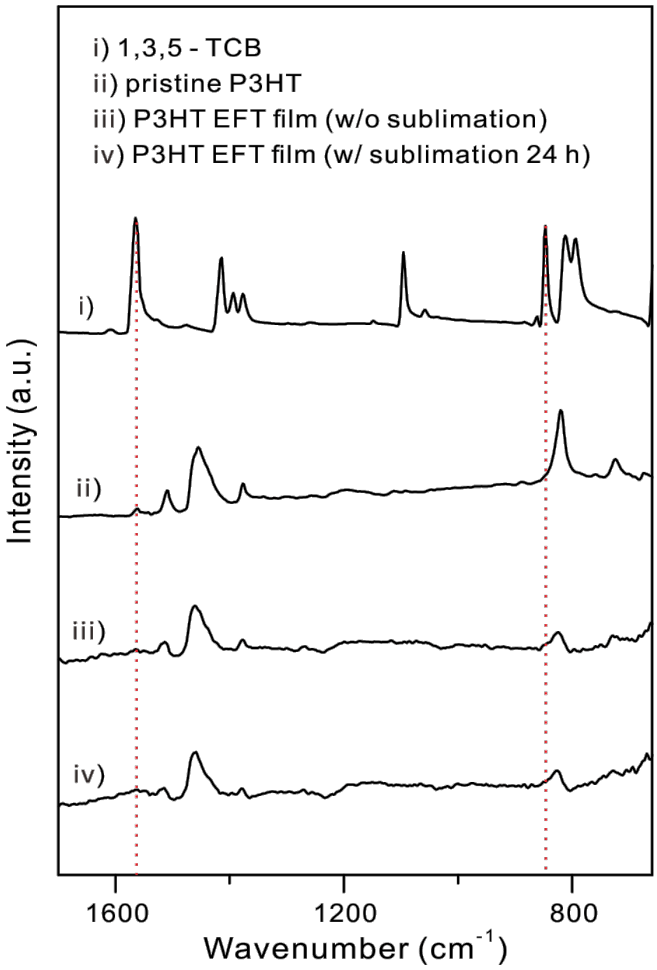

Figure S5. FT-IR spectra of i) 1,3,5-TCB, ii) pristine P3HT, iii) P3HT EFT film without vacuum sublimation and iv) P3HT EFT film with vacuum sublimation for 24 hr. The characteristic C=C stretching peak (1560 cm^{-1}) and C-Cl stretching peak (850 cm^{-1}) of 1,3,5-TCB disappeared right after EFT process. Both FT-IR spectra of EFT and vacuum sublimated one are almost identical, which shows that 1,3,5-TCB was completely removed during the EFT without additional purification process.

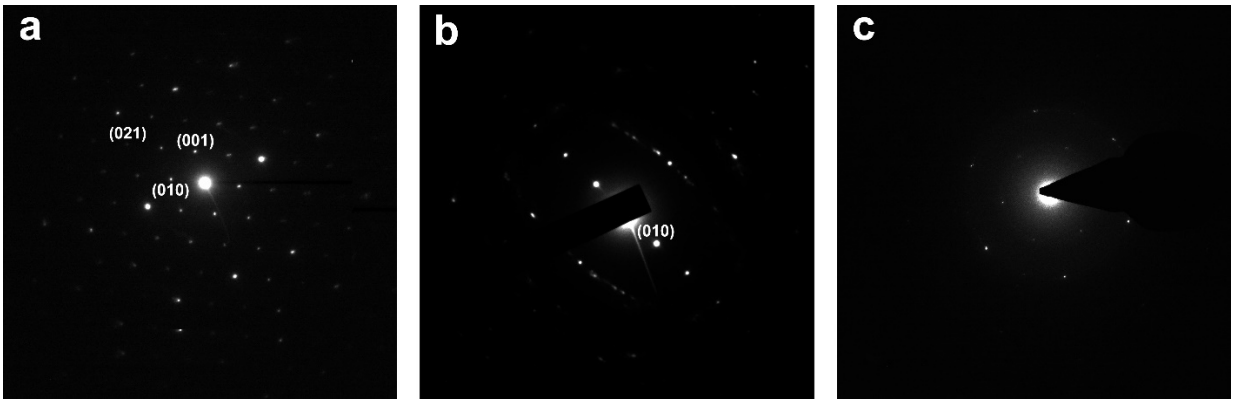

Figure S6. SAED micrographs of a) $PCDTPT_{EFT}$, b) PFT_{EFT} and c) $F8T_{EFT}$.

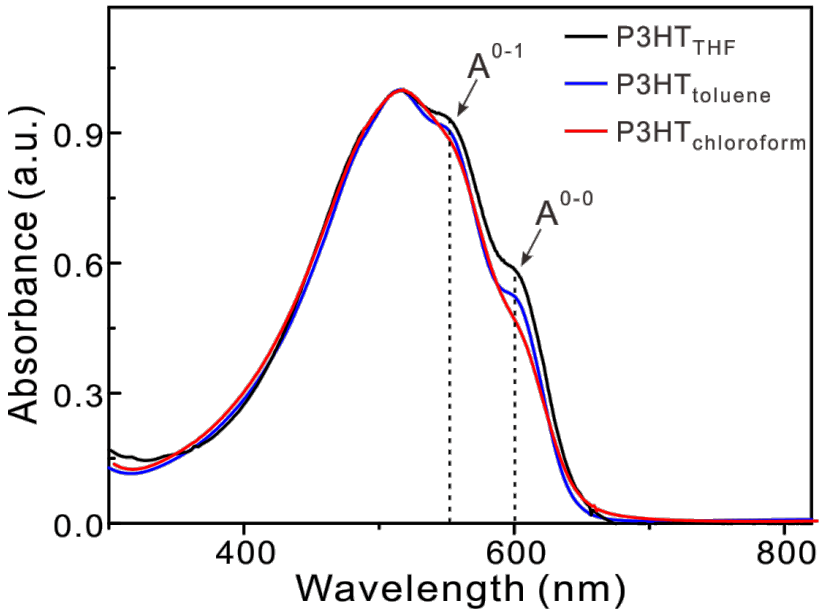

Figure S7. UV-VIS spectra of spin-casted P3HT film with THF (black solid line), toluene (blue solid line) and chloroform (red solid line). I_A^{0-0} / I_A^{0-1} ratio is 0.62, 0.56, 0.41 and exciton bandwidth is 127, 150, 225 meV, respectively.

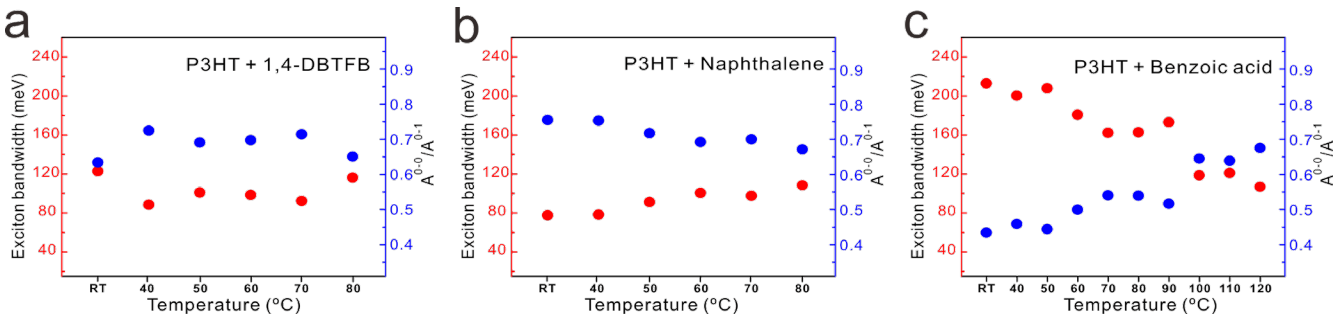

Figure S8. I_A^{0-0} / I_A^{0-1} ratio and exciton bandwidth of various matrix including (a) 1,4-DBTFB, (b) naphthalene and (c) benzoic acid.

The I_A^{0-0}/ I_A^{0-1} ratio increased in the order of benzoic acid < 1,4-DBTFB < naphthalene < 1,3,5-TCB for EFT films prepared at the substrate temperature (T_{sub}) of 25 °C. Interestingly, this order is opposite to that of the (eutectic) melting temperature of matrixes. The melting temperature of 1,3,5-TCB, naphthalene, 1,4-DBTB and benzoic acid is T_m = 65 °C, 80 °C, 83 °C and 120 °C, respectively. Since our experiments have been done at the room temperature (or at the slightly elevated temperature ~55 °C), the eutectic melting process would be more favorable for the matrix having the lower eutectic temperature. Because of this, the I_A^{0-0}/ I_A^{0-1} ratio for benzoic acid gradually increased with temperature, and became comparable that for 1,3,5-TCB at high temperature.

Additionally, the crystal structure of matrix can affect the I_A^{0-0}/ I_A^{0-1} ratio. It is known that 1,3,5-TCB crystal form epitaxy with P3HT.[1,2]

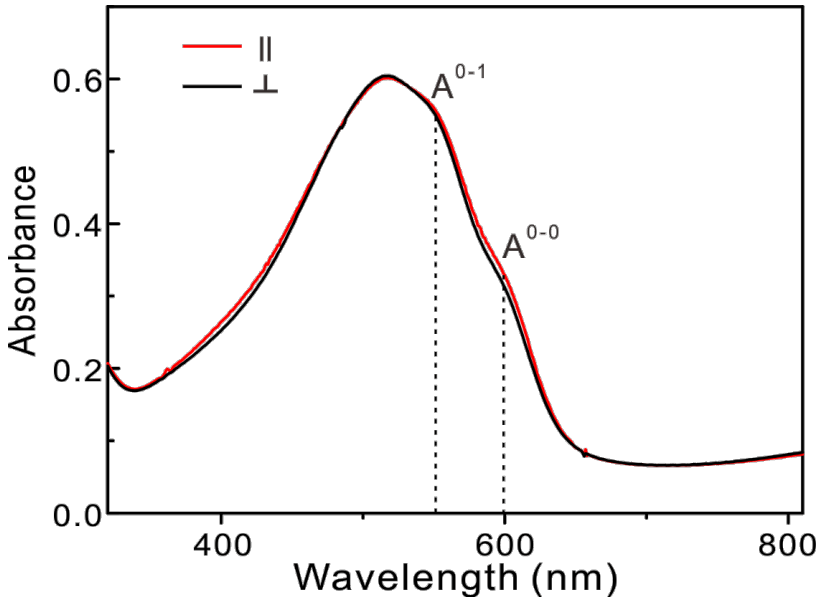

Figure S9. Polarized UV-VIS spectra of the spin-casted P3HT film. The red and black solid lines were obtained when polarization is parallel and perpendicular to the initial film position, respectively. Dichroic ratio of the spin-casted film was ~1.0, and which suggests that P3HT chains are randomly oriented.

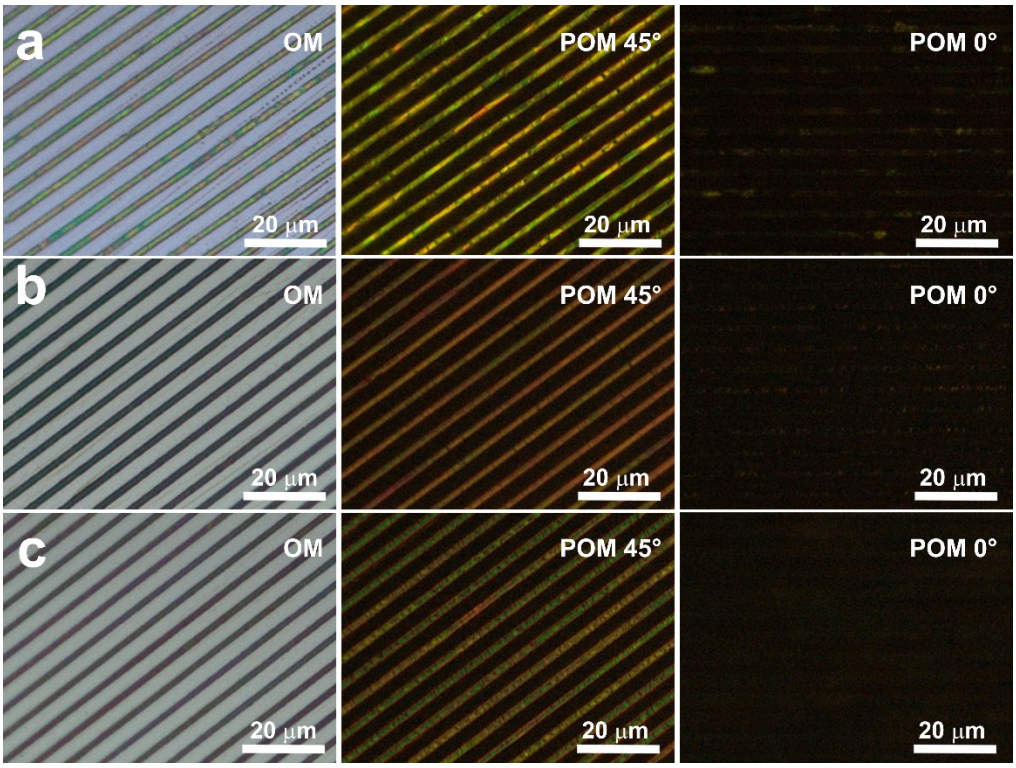

Figure S10. Micropatterns of (a) $F8BT_{EFTL}$, (b) $PCDTPT_{EFTL}$ and (c) $PFT100_{EFTL}$. (Left) optical micrograph, polarized optical micrograph when the drawing direction is (middle) 45 ° or (right) parallel to the polarizer.

Table S1. I_A^{0-0}/I_A^{0-1} and excition bandwidth of $P3HT_{EFT}$ according to matrix and processing temperature.

	1,3,5 - TCB		1,4 – DBTFB		Naphthalene		Benzoic acid	
	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)
R.T.	0.76	74.9	0.63	122	0.76	77	0.43	212
40 ºC	0.75	77.0	0.72	88	0.75	78	0.45	200
50 ºC	0.77	73.2	0.69	100	0.72	91	0.444	207
55 ºC	0.78	69.0						
60 ºC	0.74	83.0	0.70	98	0.69	100	0.50	180
65 ºC	0.71	94.0						
70 ºC			0.71	92	0.70	97	0.54	162
80 ºC			0.65	116	0.67	108	0.53	163
90 ºC							0.51	173
100 ºC							0.64	118
110 ºC							0.63	120
120 ºC							0.67	106

Table S2. I_A^{0-0}/I_A^{0-1} and excition bandwidth of $P3HT_{EFT}$ with polarized light which is parallel and perpendicular to the drawing direction.

	Perpendicular		Parallel	
	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)
$P3HT_{EFT}$	0.61	131	0.87	37
Spin-caste film	0.49	181	0.53	164

Table S3. I_A^{0-0}/I_A^{0-1} and excition bandwidth of $P3HT_{EFT}$ according to solvent.

	Chloroform		THF		Toluene	
	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)	I_A^{0-0}/I_A^{0-1} ratio	Exciton bandwidth (meV)
R.T.	0.41	225	0.58	122	0.51	77

References

1. Qu, Yao, Wang, Chen, Xu, Zeng, Shi, Zhang, Uher and Chen, *NPG Asia Mater.*, 2016, **8**, e292-e292.
2. Brinkmann and Wittmann, *Adv. Mater.*, 2006, **18**, 860-863.