SUPPORTING INFORMATION

Solvent Evaporation Induced Liquid Crystalline Phase in Poly(3-hexylthiophene)

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A. *In situ* Measurement of Drain Current

We fabricated two-contact devices in which P3HT solution is deposited on a 200 nm thick SiO$_2$ gate dielectric. A highly doped silicon wafer served as a gate electrode, and source and drain electrodes were patterned using photolithography with the channel length of 15 to 165 µm and the width of up to 2 mm. P3HT solution with a concentration of 5 mg/mL was prepared using 1,2,4-trichlorobenzene (TCB). A droplet of the P3HT solution was carefully deposited onto the device so that the center of the droplet can be positioned on the channel. Upon solution deposition, we measured the source-drain current in air at a particular gate voltage until the P3HT solution formed a solid film.
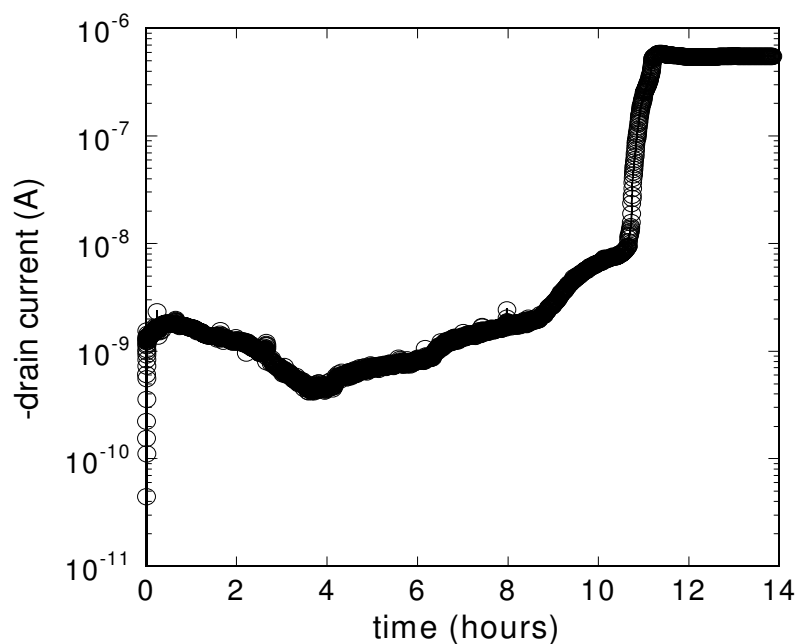

Figure S1. Time evolution of the drain current in a field effect transistor (FET) where P3HT solution with 1,2, 4-Trichlorobenzene (TCB) was deposited. For the FET devices, gate and drain voltages was fixed at -10 and -5 V, respectively.

B. Experimental Setup for Polarized Raman Spectroscopy

Polarized Raman spectra were obtained using a 10× objective and a 785 nm laser light source (Kaiser Optic System) which has 4 cm^{-1} resolution in the backscattering geometry. The illuminated sample area was estimated to be about 15 µm in diameter and the laser power was limited to 30 mW to avoid local degradation of the sample. The polarized component (I_{ll}) was obtained by setting the analyzer parallel to the polarization direction of the incident beam. The anisotropic nature of P3HT chains was elucidated by recording a series of polarized Raman spectra as a function of angle, θ, between the polarization vectors of incident light and the symmetry axis of P3HT backbone. In order to obtain any combination of θ, we rotated the sample stage against polarization direction of the incident beam. Angular dependence was detected by measuring polarized Raman spectra at every 15º from 0º to 90º and we arbitrarily fixed θ = 90º as the angle at which Raman peak is most intense and background fluorescence arises.

In order to track the variation of peak position and shape as a function of evaporation time, we continuously measured the Raman spectra by accumulating the signal for 3 seconds with 5 time repetitions just from depositing a solution drop until evaporation is completed. Although each spectrum was acquired with fixed time interval (15 sec), i.e., not simultaneously, this time interval is so short in comparison to the time scale of complete solvent evaporation that we can ignore the influence of time difference on peak spectra between consecutively measured spectra. The experimental setup with a backscattering configuration is shown in Scheme S1.
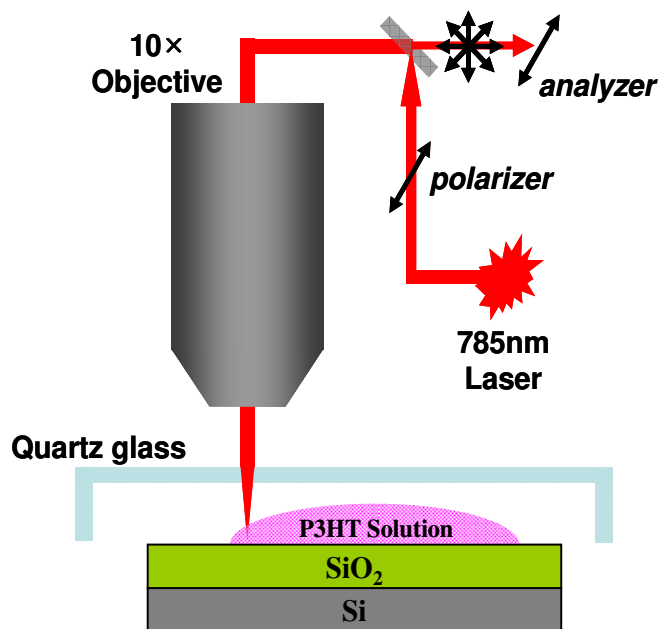
Scheme S1. Experimental setup for in-situ polarized Raman scattering measurement in back scattering geometry.
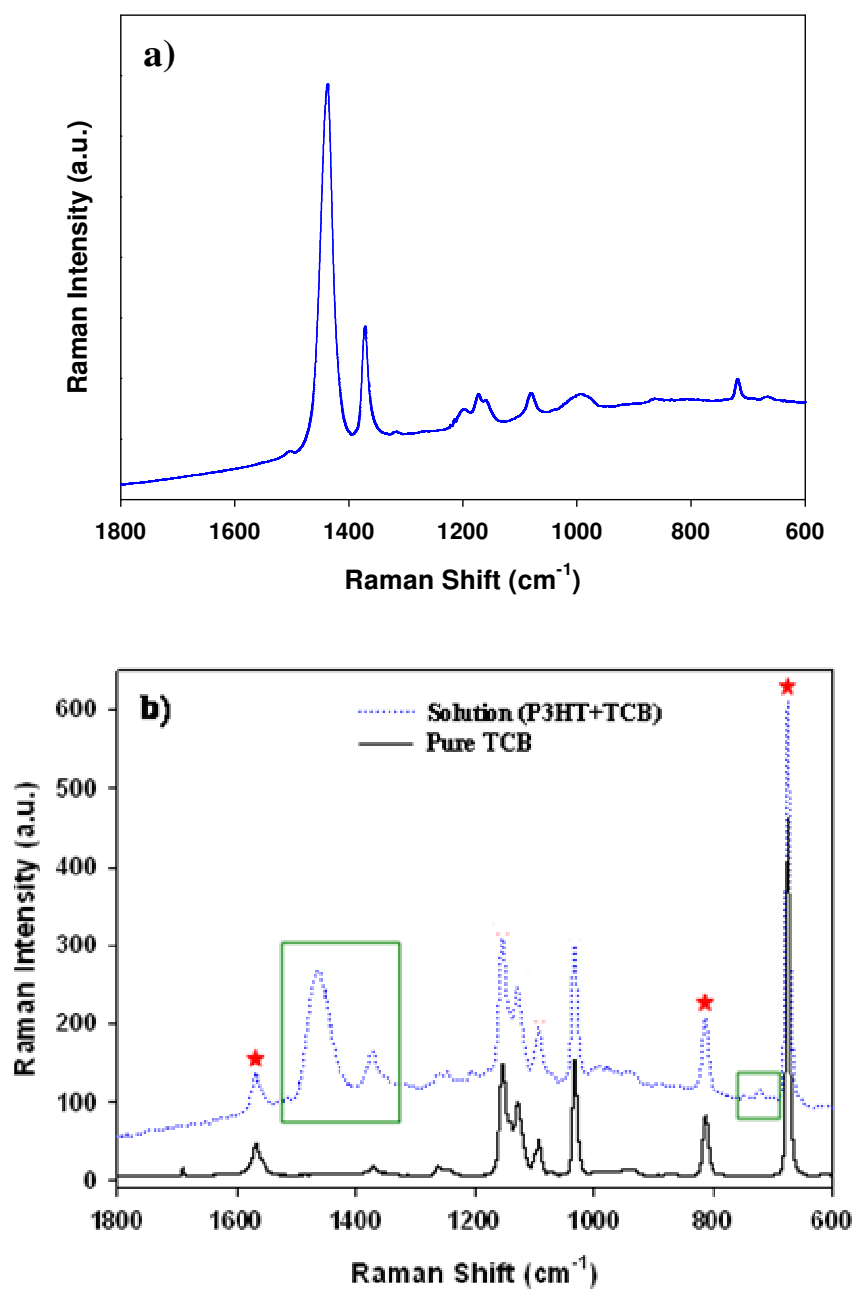
C. Analysis of Polarized Raman Spectra

C. 1. Peak Assignments in Pure P3HT

Polarized Raman spectra in 600-1800 cm^{-1} region are plotted for pure P3HT in Figure S2(a), pure 1,2,4-TCB, and P3HT solution with 1,2,4-TCB in Figure S2(b). It is always quite complicated and not definite to assign vibration bands. Nevertheless, we assigned the most intense peak at 1443 cm^{-1} to symmetric $C_\alpha=C_\beta$ stretching band in thiophene rings, a characteristic band which reflects the structural change in thiophene backbone, based on the results in previous literature: (1) Raman spectra of both polythiophene without alkyl substitution and poly(3-alkylthiophene) are mainly composed of a large band peaked near 1450 cm^{-1}, implying this band is independent of alkyl substitution.[1] (2) The vibration

frequency of this band varies according to the number of thiophene rings, i.e., the extent of conjugation, which has been determined by experimental observation as well as calculation of vibrational frequencies.[2-4] (3) Oxidative doping of thiophene oligomers[5] and a poly(3-alkylthiophene)[4] exhibits obvious changes in both position and shape of this peak, which means this band is associated with the existence of the π-bonding system. (4) The position of strong and characteristic Raman bands in alkyl chain categorized as *C-H* stretching and skeletal stretching (*C-C*) have been well known to be in the regions of 2800-3000 cm^{-1} [6-8] and under 1200 cm^{-1} [8,9], respectively.

In Figure S2(b), Raman peaks of 1,2,4-TCB, distinct from those of pure P3HT, are highlighted with star marks (□). Especially, the most intense peak (with about 8 cm^{-1} FWHM) at 677 cm^{-1} contributed to *C-Cl* stretching vibration[10] can be used as an indicator of the existence of non-negligible amount of solvent. Raman spectra measured between 630 minutes and 675 minutes after depositing a drop clearly show the peak at 677 cm^{-1} and the FWHM of these peaks are about 8 cm^{-1} in Figure S3. For the spectra measured after 675 minutes to 720 minutes, it is difficult to differentiate this peak from spectra due to continuous evaporation of solvent and very strong background fluorescence. However, meticulous spectra analysis enables us to detect that there remains more solvent even until 720 minutes than the amount in dried film.

Figure S2. (a) Polarized Raman spectra of pure P3HT powder, and (b) polarized Raman spectra of P3HT solution in TCB as well as pure TCB, under parallel polarization mode (I_{ll}) at 30℃. Peaks highlighted with star mark (□) are characteristic Raman bands of pure solvent, 1,2,4-TCB and peaks in green square are contributed to the vibrations of pure P3HT.
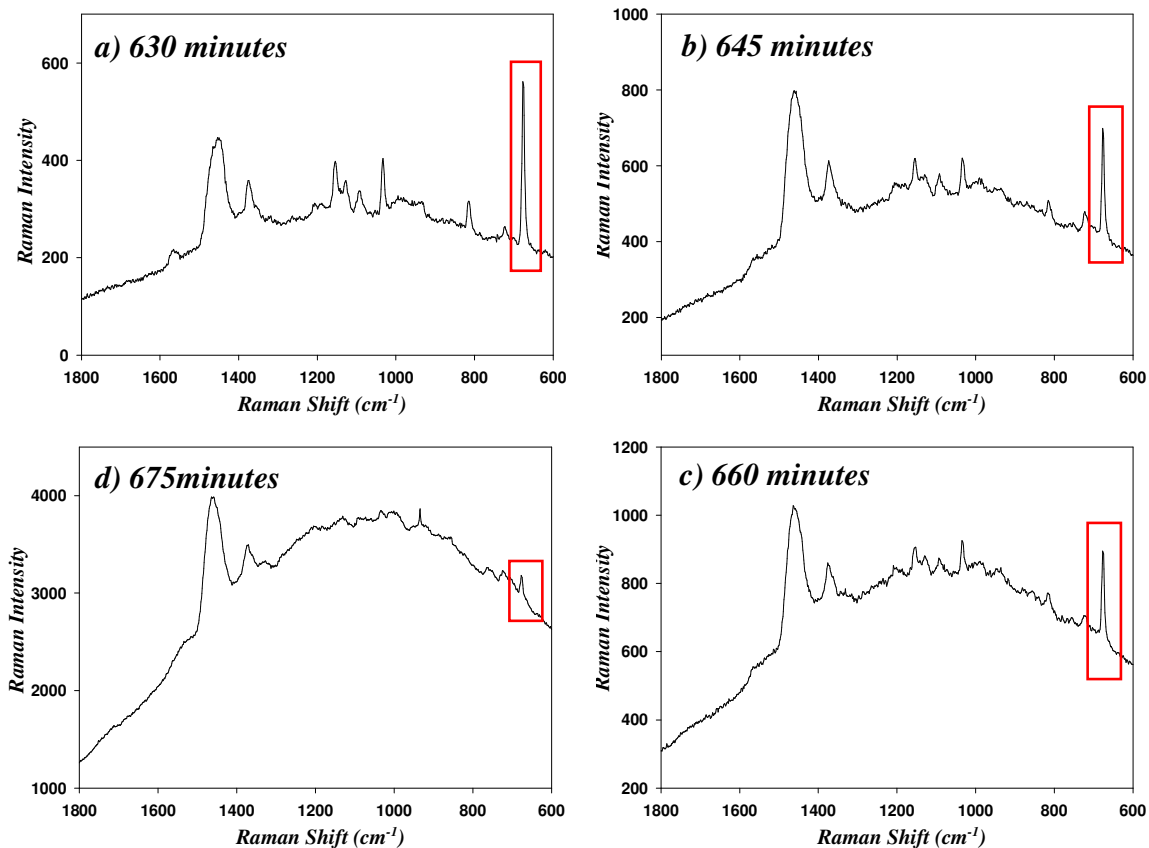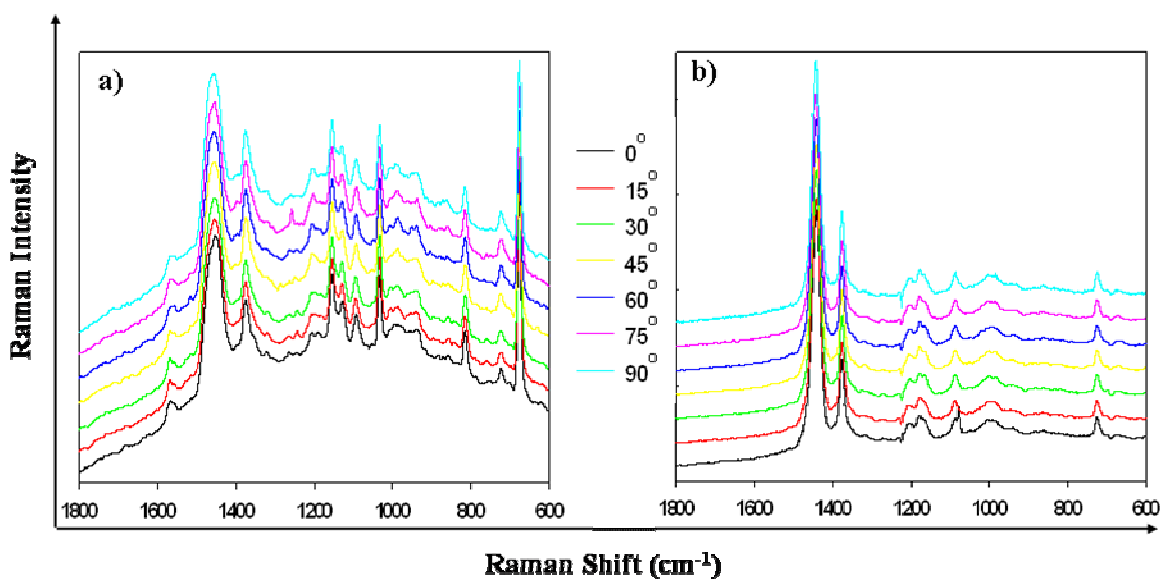
Figure S3. Polarized Raman spectra measured at 630~675 minutes, when polarized Raman intensities exhibit anisotropic nature. In all spectra, a distinct peak at 667 cm^{-1} assigned to only pure 1,2,4-TCB is clearly detected as shown within red squares.

C. 2. Angular Dependence of Polarized Raman Intensity
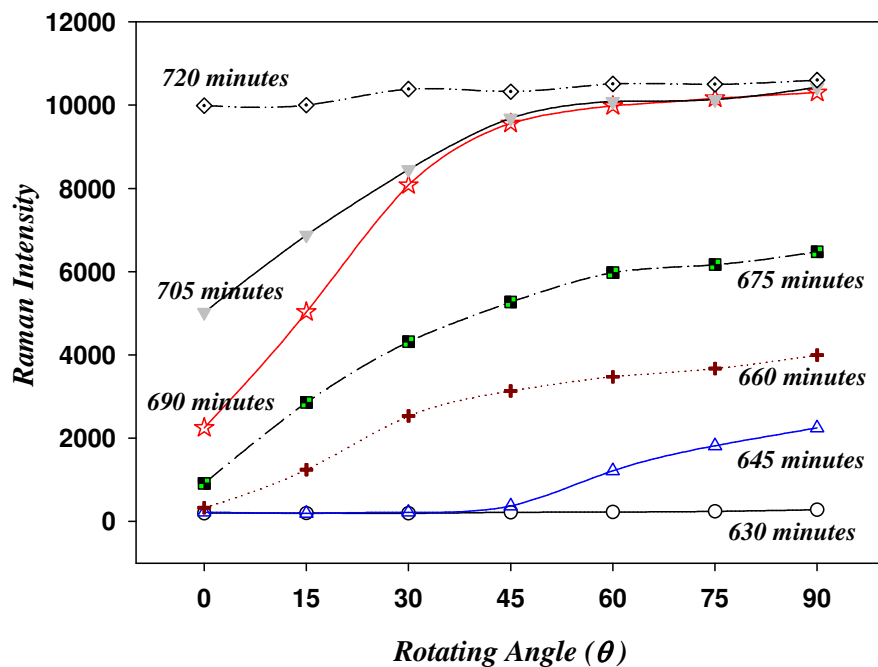
Figure S4. Time evolution of angular dependence of polarization intensity of Raman peak of symmetric *C=C* stretching, $I_{C=C,}$ between 630 minutes and 720 minutes. Outside of these time scale, i.e., for 0~630 minutes and 720 ~1200 minutes, there is no angular dependence and thus the ratios of $I_{C=C}$ for 0° and 90° are one over the entire time.

Figure S5. Plots of polarized Raman spectra consecutively measured by rotating sample stage at: (a) 30 minutes (isotropic solution state), and (b) 800 minutes (dried film state) after deposition, respectively. Spectra in figures are intentionally shifted for a lucid comparison. Otherwise, all spectra in each state are identical.

C. 3. Optical Anisotropy at the Edge of the 3-phase Contact Line
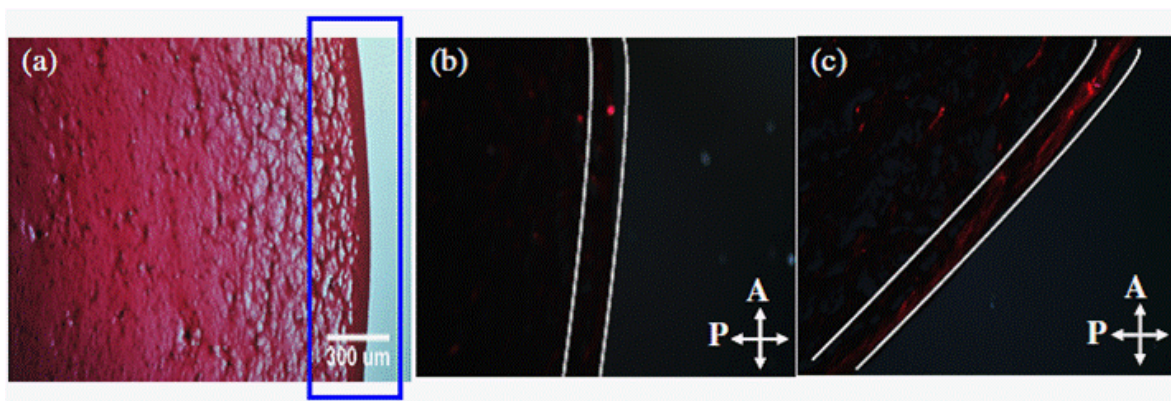
Figure S6. (a) Optical microscopic image (10×) of ring-like edge area of the film deposited by evaporation of P3HT solution. The diameter of drop is approximately 5 mm. (b) and (c) The images of the same film (20×) in the vicinity of perimeter under crossed polarization, when the direction of outward flow of solvent is parallel (b) and 45° tilted (c) to the polarizer.

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