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Large-Scale Highly Ordered Hierarchically Structures of Conjugated Polymer via Self-Assembly from Mixed Solvents**

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Experimental Section

Materials and preparation

Regioregular P3HT (Mw = 45000 Da, PDI = 2.0, RR = 98%) was purchased from Rieke Metals Inc. and used without further purification. P3HT solutions in different solvents were prepared with the concentration of P3HT at 0.1 mg mL^{-1}. The Si (or SiO_2) substrates (1.5 cm × 1.5 cm) and cylindrical lenses (L = 12 mm, W = 10 mm, R = 12.92 mm) were cleaned with a *piranha solution* (7:3 98% H_2SO_4/30% H_2O_2) at 80 °C for 2 h to remove stains on the surface (Caution! *Piranha solution* reacts violently with organic materials.), then washed thoroughly with deionized water and dried under nitrogen flow. Cylindrical lenses were situated on a Si flat substrate to construct the cylinder-on-flat geometry in Scheme 1. P3HT solution (30 μL) was trapped within the gap between the cylinder and substrate due to the capillary force. After evaporation, patterns were produced on flat substrates.

Characterization

The assembled patterns were observed by a Carl Zeiss A1m microscope with a charge-coupled device camera. AFM characterization was obtained on an Agilent 5500 AFM by tapping mode in an ambient atmosphere. Orientation of P3HT Chains

were obtained as in previous report.[10] Raman spectra were obtained with LabRam HR800 spectrometer (Horiba Jobin Yvon) equipped with an Olympus BX41 microscope in the backscattering geometry. Both the confocal hole and the slit width were fixed at 200 μm. A 632.8 nm He–Ne laser was focused on the sample with a 50X objective lens (0.75 NA). The spatial resolution of the beam spot is around 1 μm. The power at the sample was ~ 1.8 mW. A half-wave plate was used to select the polarization of the incident laser beam and a polarizer was used to select polarization of the scattered beam. A scrambler was placed before the 600 groove/mm holographic grating in order to minimize its polarization-dependent response. Stripes were aligned along the *Z* direction and polarized spectra were recorded in the order: *ZZ*, *XX*. Ratios were obtained by measuring ten different points in one stripe in the outer region. Electrical conductivity was measured using a Keithley 236 source meter. TEM was carried out on a JEOL JEM-1011 electron microscope operating at an acceleration voltage of 100 kV. Gas Chromatography was performed on GC-14C Chromatography from SHIMADZU.

Table S1. The boiling point (*T*b), surface tension (γ), and solubility parameter (δ) of solvents applied. Data compiled from Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds © 2003 Knovel.

Solvents	**b.p.[℃]**	**γ[mn m^{-1}]**	**δ[(cal cm^{-3})$^{1/2}$]**
Chloroform (CF)	61.18	26.68	9.30
Methylbenzene (MB)	110.63	27.93	8.97

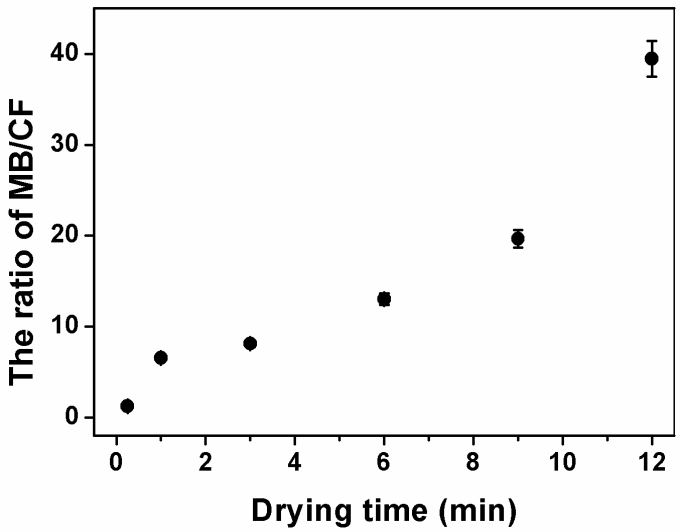

Figure S1. The ratio changing of MB/CF of fresh prepared P3HT in CF/MB 1/1 solution as a function of time during the drying process.

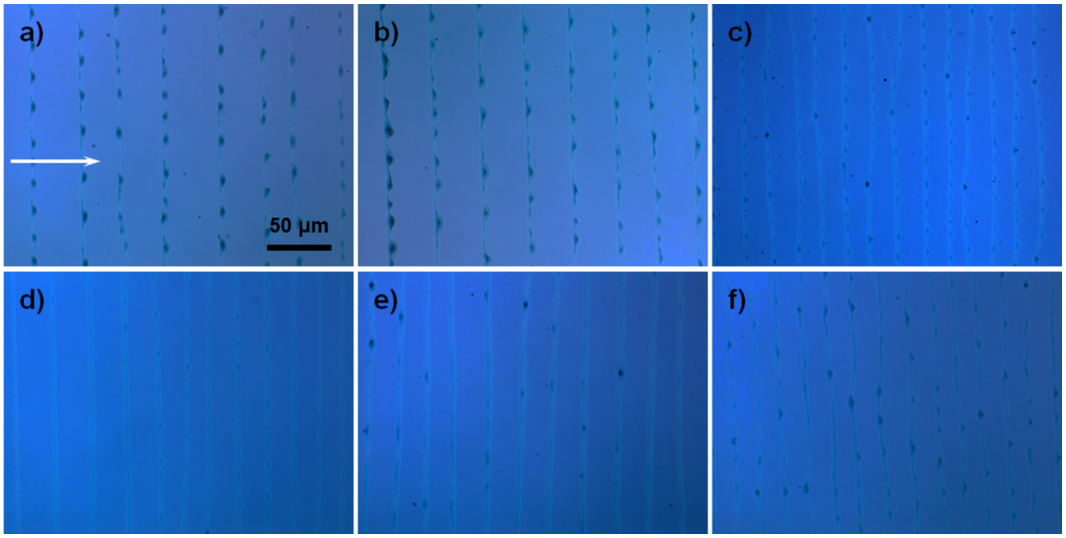

Figure S2. OM images of P3HT stripe patterns in the outer region from 0.1 mg/mL P3HT in solvents with different volume fractions of methylbenzene. a) 20%, b) 30%, c) 40%, d) 60%, e) 70% and f) 80%. The correnponding ratio of MB/CF after drying for 15 s was 2.0, 3.1, 4.9, 10.6, 15.3, 24.1, respectively. The arrow marks the movement of the solution front during evaporation.

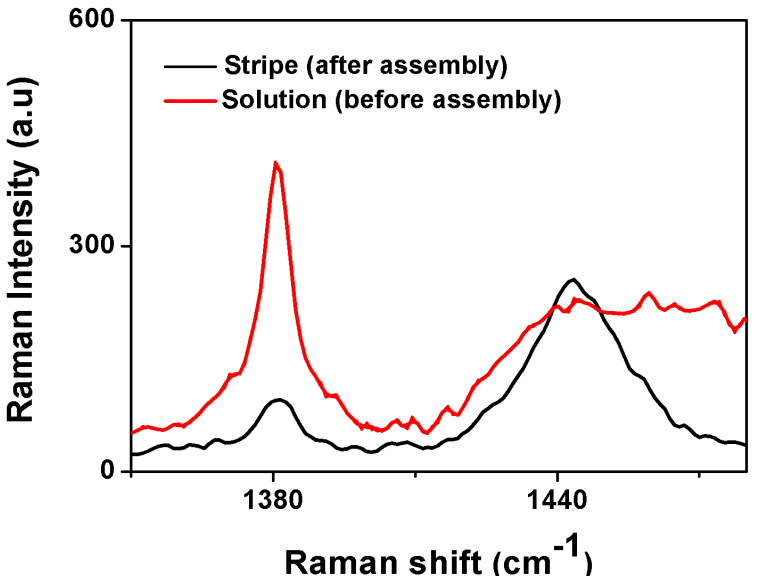

Figure S3. Raman spectra of fresh prepared P3HT dissolved in CF/MB 1/1 mixed solvents before (red line) and after self-assembly (black line).

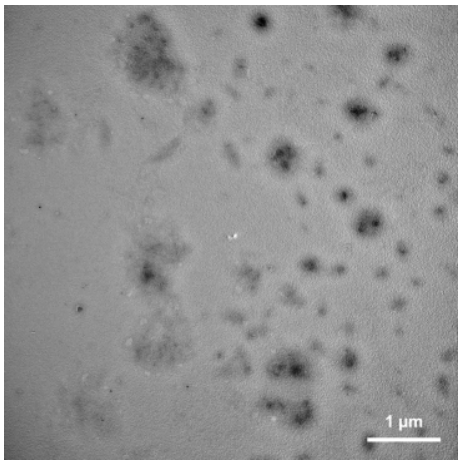

Figure S4. TEM image of fresh prepared P3HT in CF/MB 1/1 mixed solvents.

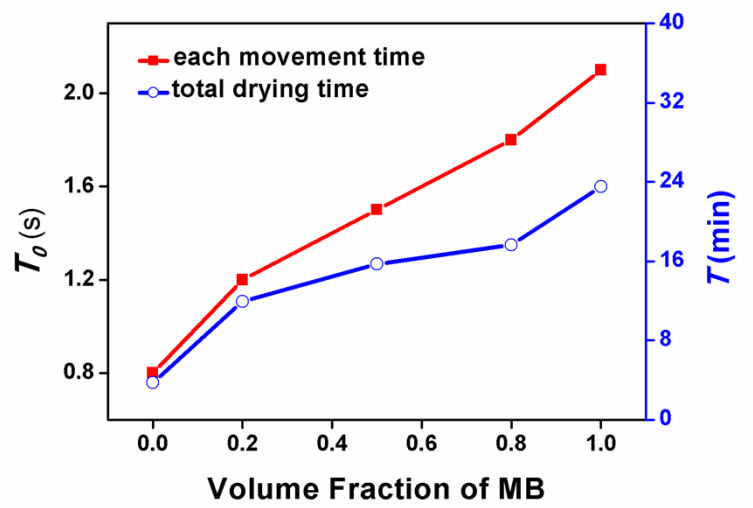

Figure S5. Total drying time (T) and each movement of time (T_0) as a function of different volume fraction of MB.