

## Supporting information

### **Direct Patterning of Poly(3-hexylthiophene) and Its Application to Organic Field-Effect Transistor**

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### Materials and characterization

Regioregular poly(3-hexylthiophene) (rr-P3HT) and 4,4'-methylenebis[2,6-bis(methoxymethyl)phenol] (MBMP) were prepared according to the previous reports [S1-S3]. Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS), other reagents and solvents were purchased from Sigma-Aldrich Co. and Tokyo Chemical Industry Co., Ltd. and used as received. FT-IR spectra were recorded on a Horiba FT-720 spectrophotometer.  $^1\text{H}$  NMR spectra were obtained in  $\text{CHCl}_3-d_1$  on a BRUKER DPX-300 spectrometer at 300 MHz.  $M_n$  and PDI were evaluated by gel permeation chromatography (GPC) on a JASCO GULLIVER 1500 system equipped with a polystyrene gel columns (Plgel 5  $\mu\text{m}$  MIXED-C) eluted with  $\text{CHCl}_3$  at a flow rate of 1.0  $\text{mL min}^{-1}$  calibrated by standard polystyrene samples. The film thickness was measured by Veeco Instrument Dektak surface profiler. The optical images were taken with Nikon ECLIPSE L150 microscope.

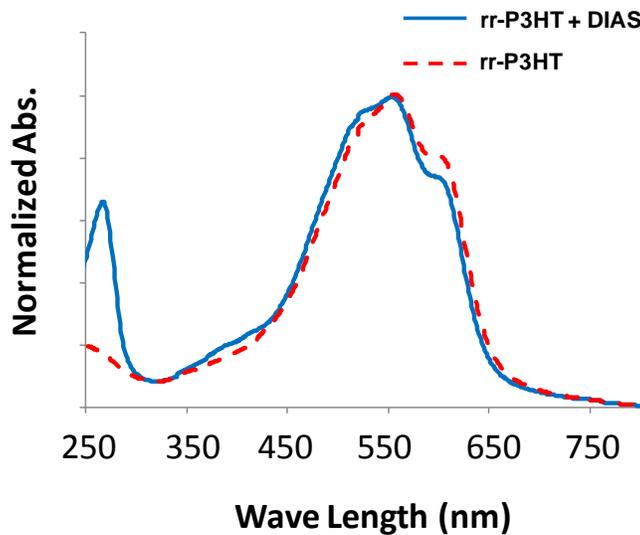
### Dissolution rate

rr-P3HT was dissolved in 1,1,2,2-tetrachloroethane (TCE), followed by addition of MBMP and DIAS. The total concentration of the TCE solution was 1 wt%. The 130-150 nm thickness of polymer films was obtained by spin-coating from the solution on a silicon wafer. These films were pre-baked at 80  $^\circ\text{C}$  for 1 min, and then exposed to a super-high pressure mercury lamp without any filters, followed by post-exposure bake (PEB) at each temperature for 1 min. The dissolution rate ( $\text{\AA}/\text{sec}$ ) of the film thickness was determined from the changes in the film thickness before and after development with chloroform.

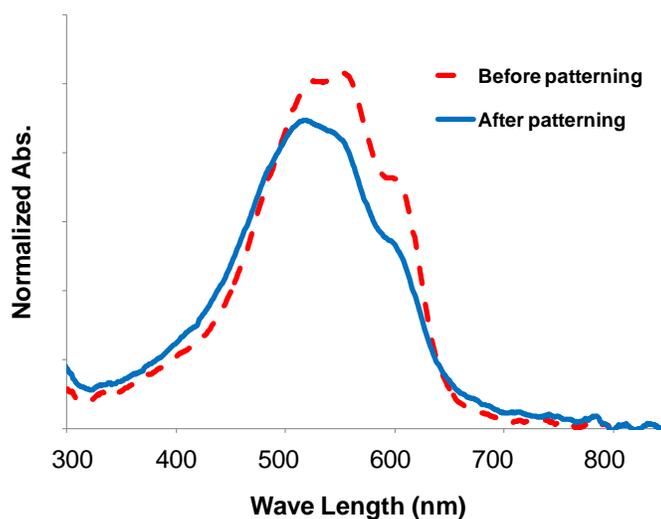
### Photopatterning of rr-P3HT

rr-P3HT was dissolved in TCE, followed by addition of MBMP and DIAS. The total concentration of the TCE solution was 1 wt%. The 100 nm thickness of polymer films was obtained by spin-coating from the solution on a silicon wafer. This film was pre-baked at 120 °C for 1 min, and then exposed to a super-high pressure mercury lamp without any filters through a photo mask for 5 min in a contact-printing mode, followed by PEB at 170 °C for 30 min. The exposed film was developed in chloroform for 1 sec to give clear patterns on the 100 nm thickness of the rr-P3HT film.

### UV-visible absorption spectra of the rr-P3HT films



(a)

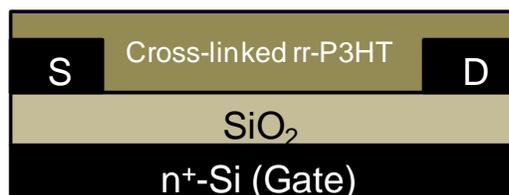


(b)

**Figure S1.** (a) UV-visible spectra of the rr-P3HT films with or without DIAS addition. The films were prepared from 1 wt% TCE solution by a spin-coating method, followed by drying at 100 °C for 1 min. DIAS (20 wt%) was mixed with rr-P3HT solution to form the blend film. (b) UV-visible spectra of the photosensitive rr-P3HT films (rr-P3HT: 85 wt%, MBMP: 10 wt%, and DIAS: 5 wt%) before and after patterning processes. The films were prepared from 1 wt% TCE solution by a spin-coating method, followed by drying at 100 °C for 1 min (before patterning, dashed line). Then the films were exposed with UV light for 5 min, post-baked at 180 °C for 1 min, and developed with chloroform, followed by additional thermal and dedoping treatments as described in the main text (after patterning, solid line).

### Fabrication and measurement of OFET

An n-doped Si substrate was used as the gate electrode with a 300 nm-thick SiO<sub>2</sub> dielectric layer (capacitance ( $C_i$ ) = 11.5 nF cm<sup>-2</sup>). For the bottom-contact and bottom-gate geometry, the gold and chromium bilayer source and drain electrodes (channel width ( $W$ ) = 500 μm and channel length ( $L$ ) = 10 μm) were photolithographically patterned onto the SiO<sub>2</sub>/Si substrate. A TCE solution of rr-P3HT (85 wt%), MBMP (10 wt%), and DIAS (5 wt%) was spin-coated on top of the substrate to form the semiconductor film (thickness = 100 nm), followed by photo-patterning of the semiconductor layer as described above. The device structure is shown in Figure S2. The patterned rr-P3HT film on the SiO<sub>2</sub>/Si substrate was heated at 200 °C for 30 min, and treated with 1 wt% aqueous ammonia solution for 30 min at room temperature, followed by thermal annealing at 180 °C for 30 min. OFET measurements were performed under dry N<sub>2</sub> atmosphere. Current-voltage characteristics were obtained with a semiconductor parameter analyzer.  $I$ - $V$  characteristics of bottom-contact OFET devices using spin-coated and patterned rr-P3HT as the semiconductor layer are shown in Figure 4 in the main text.



**Figure S2.** Schematic image of bottom-contact and bottom-gate OFET

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- (S2) R. Miyakoshi, A. Yokoyama and T. Yokozawa, *J. Am. Chem. Soc.* 2005, **127**, 17542.
- (S3) K. Mizoguchi and M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* 2008, **46**, 4949.