Supporting information

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

Yuta Saito, a Yoshimasa Sakai, b Tomoya Higashihara, a and Mitsuru Ueda* a

a Department of Organic and Polymeric Materials, Tokyo Institute of Technology
2-12-1-H120 O-okayama, Meguro-ku, Tokyo, Japan 152-8552

b Mitsubishi Chemical Group, Science and Technology Research Center, Ink.
1000 Kamoshida-cho, Aoba-ku, Yokohama, Japan 227-8502

Corresponding author email: ueda.m.ad@m.titech.ac.jp
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]. Diphenyldonium 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. $^1$H NMR spectra were obtained in 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 μm MIXED-C) eluted with CHCl$_3$ at a flow rate of 1.0 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 °C for 1 min, and the 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 (Å/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 the 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)
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 patternning 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$_2$ dielectric layer (capacitance ($C_i$) = 11.5 nF cm$^{-2}$). 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$_2$/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$_2$/Si substrate was heated at 200 ºC for 30 min, and treated with 1 wt% aqueous ammonia solution for 30 min at room temperature, followed by thermal annealing at 180 ºC for 30 min. OFET measurements were performed under dry N$_2$ 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](image-url)
