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Controlled Nanomorphology of PCDTBT/Fullerene Blends via Polymer End-group Functionalization for High Efficiency Organic Solar Cells

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Polymerization

Polymerization of H-terminated PCDTBT

526.08mg (0.8mmol) of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 366.56mg (0.8mmol) of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole, 3.7mg (0.004mmol) of tris(dibenzylideneacetone)dipalladium (0) and 4.9mg (0.016mmol) of tri(o-tolyl)phosphine were added in the argon environmental three-neck flask. 10ml of toluene and 3.4ml of 20% (w/w) aqueous tetraethylammonium hydroxide were degassed and added to the flask. The reaction mixture was refluxed for 225min. 157mg (1mmol) of bromobenzene was added to the reaction mixture and reaction mixture was refluxed for 1 day. Solution of phenylboronic acid (144mg, 1.2mmol) and toluene (5ml) was added to the reaction mixture. After additional 1 day, reaction mixture was poured out 500ml of methanol and polymer was filtered out. The crude polymer was washed acetone, hexane, dichloromethane and chloroform using soxhlet extraction. Chloroform soluble polymer was quenched in the methanol, filtered and dried under vacuum oven. GPC analysis $\overline{M}_n = 12.3K$, $\overline{M}_w = 52.3K$, PDI = 4.25

Polymerization of CF₃-terminated PCDTBT

526.08mg (0.8mmol) of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 366.56mg (0.8mmol) of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole, 3.7mg (0.004mmol) of tris(dibenzylideneacetone)dipalladium (0) and 4.9mg (0.016mmol) of tri(o-tolyl)phosphine were added in the argon environmental three-neck flask. 10ml of toluene and 3.4ml of 20% (w/w) aqueous tetraethylammonium hydroxide were degassed and added to the flask. The reaction mixture was refluxed for 225min. 225mg (1mmol) of 1-bromo-4-(trifluoromethyl)benzene was added to the reaction mixture and reaction mixture was refluxed for 1 day. Solution of 4-(trifluoromethyl)phenylboronic acid (228mg, 1.2mmol) and toluene (5ml) was added to the

reaction mixture. After additional 1 day, reaction mixture was poured out 500ml of methanol and polymer was filtered out. The crude polymer was washed acetone, hexane, dichloromethane and chloroform using soxhlet extraction. Chloroform soluble polymer was quenched in the methanol, filtered and dried under vacuum oven. GPC analysis $\overline{M}_n = 11.0K$, $\overline{M}_w = 59.9K$, PDI = 5.44

Polymerization of OH-terminated PCDTBT

526.08mg (0.8mmol) of 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, 366.56mg (0.8mmol) of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole, 3.7mg (0.004mmol) of tris(dibenzylideneacetone)dipalladium (0) and 4.9mg (0.016mmol) of tri(o-tolyl)phosphine were added in the argon environmental three-neck flask. 10ml of toluene and 3.4ml of 20% (w/w) aqueous tetraethylammonium hydroxide were degassed and added to the flask. The reaction mixture was refluxed for 225min. 173mg (1mmol) of 4-bromophenol was added to the reaction mixture and reaction mixture was refluxed for 1 day. Solution of 4-hydroxyphenylboronic acid (166mg, 1.2mmol) and toluene (5ml) was added to the reaction mixture. After additional 1 day, reaction mixture was poured out 500ml of methanol and polymer was filtered out. The crude polymer was washed acetone, hexane, dichloromethane and chloroform using soxhlet extraction. Chloroform soluble polymer was quenched in the methanol, filtered and dried under vacuum oven. GPC analysis $\overline{M}_n = 15.5K$, $\overline{M}_w = 32.8K$, PDI = 2.12

Device Fabrication

The end group terminated PCDTBT and PCBM blend solutions (1:4) were prepared in dichlorobenzene at a concentration of 7mg/ml. The devices were fabricated on top of ITO-coated substrates. The ITO coated glass was cleaned by detergent, water, acetone and ethanol with an ultrasonication. After 10min of the ozone treatment, a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron, PTP 4083, Bayer AG) was spin-coated on the ITO coated glass to a layer with a thickness of 30~50nm. And then PEDOT:PSS coated glass is dried in the oven at 120 °C for 1h. The photoactive layer was spin-coated on the PEDOT:PSS layer. Before metal deposition, the devices were dried at 90 °C for 10min. Finally, LiF (0.6nm) / Al (80nm) cathodes were thermally deposited. The current density-voltage (J-V) characteristics were measured by using Keithley 4200 source under AM 1.5 solar illumination (Oriel 1kW solar simulator) with respect to the reference cell PVM 132

(calibrated at the National Renewable Energy Laboratory). The optical spectra were acquired using Cary 5000 UV-Vis spectrometer (Varian)

Characterization

We characterized end terminated PCDTBT by using IR and ^{19}F -NMR as shown in Figure S1. We can verify the infrared peak of the trifluorophenyl group at the 1125nm wavelength and the infrared peak of the phenol group at the 1360nm wavelength.^[11] We double-checked the existence of the fluorine atom to use the ^{19}F -NMR peak ($\delta = -61.25$). At the result, end group functionalization work well.

Cyclic Voltammetry Analysis of the End Functional PCDTBT

We used cyclic voltammetry to verify that the end group functionalizations do not significantly change the polymers' electrochemical band gaps. From the Figure S2, the highest occupied molecular orbital and lowest unoccupied molecular orbital levels of the end group modified polymers are similar to those of pristine PCDTBT, i.e., 5.5 eV and 3.6 eV respectively

Transmission Electron Microscope (TEM) Analysis of the End Functional PCDTBT

We visualize the morphologies of the end-modified PCDTBT films and CF_3 -PCDTBT has distinctly fibrous structures as shown in Figure S3.

Grazing incidence X-ray diffraction (GIXRD) Experiments

Grazing incidence X-ray diffraction (GIXRD) experiments were performed using the 3D beamline (incident angle: 0.18° , 1D out of plane) at the Pohang Accelerator Laboratory (PAL). The GIXRD measurements were obtained in a scanning interval of 2θ between 3° and 27° with the monochromatic radiation of the X-ray wavelength of 1.54 \AA .

DSC Experiments

We gained the DSC data to show the ordered phase of end-group functionalized PCDTBTs. H- and OH-PCDTBT do not contain the crystallization peaks, whereas there is a small, but sharp melting and crystallization peak around 260°C for the CF_3 -PCDTBT as shown in Figure S4. This tendency is similar to our GIXRD data, which only CF_3 -PCDTBT has the GIXRD pattern at the $2\theta = 5$. These results indicate that CF_3 -PCDTBT has higher ordering

than other polymers. The rates were 10 °C/min.

Device Optimization by the Thickness of the Film

We demonstrated the preparation of the organic solar cells with efficiencies of 6.02% (average value) by using end group functionalized PCDTBT: PCBM without post treatments, additives and optical spacers. For high efficiency organic solar cells, we optimized the device by the thickness of the film as shown in Figure S5

Calculation of Jsc from IPCE data

The external quantum efficiency of the device is defined as the ratio of the collected electrons to the incident photons. Jsc is calculated as

$$J_{SC} = \frac{hc}{q} \int_{\lambda_1}^{\lambda_2} \frac{P_{AM1.5G}(\lambda) * EQE(\lambda) * d\lambda}{\lambda}$$

where h is Planck's constant (J/s), c is the speed of light in vacuum (ms^{-1}), and λ_1 and λ_2 (nm) are the limits of the active spectrum of the device. (G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* 2009, 21, 1323.)

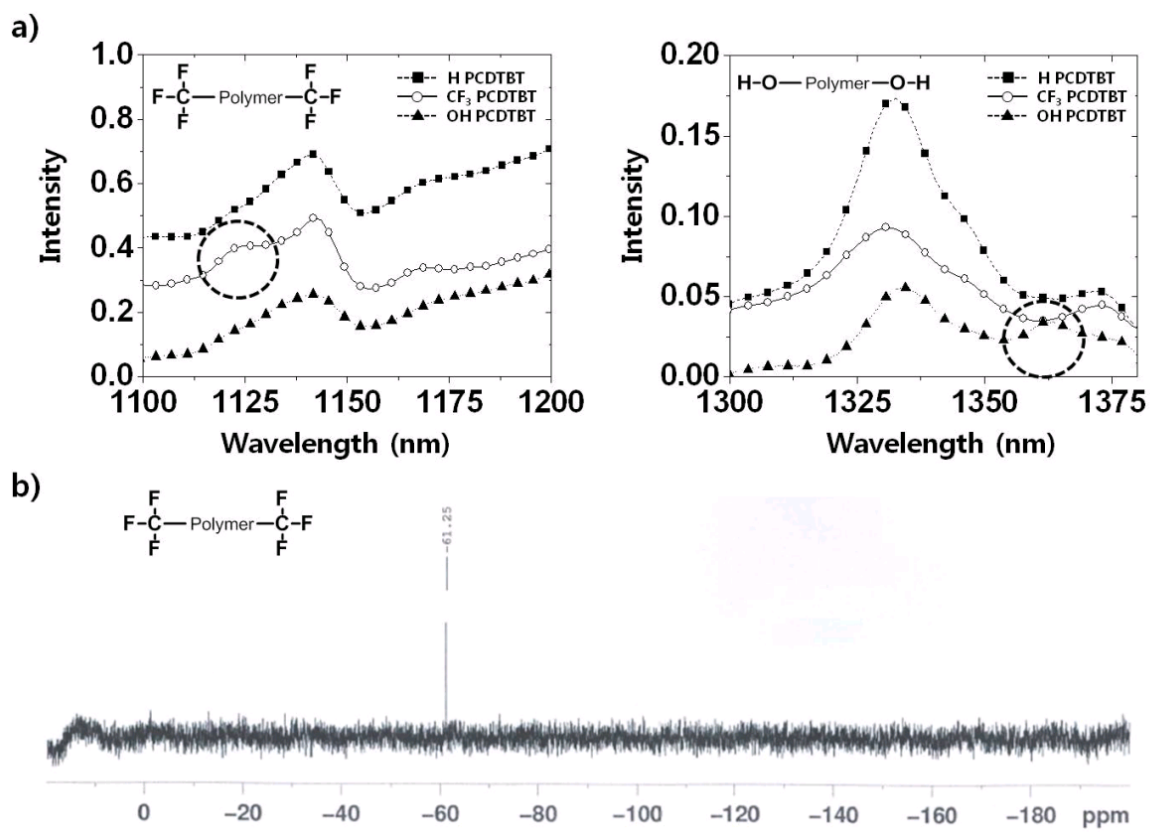


Figure S1. a) IR spectroscopy data of the end group functionalized PCDTBT b) ^{19}F - NMR data of CF_3 terminated PCDTBT

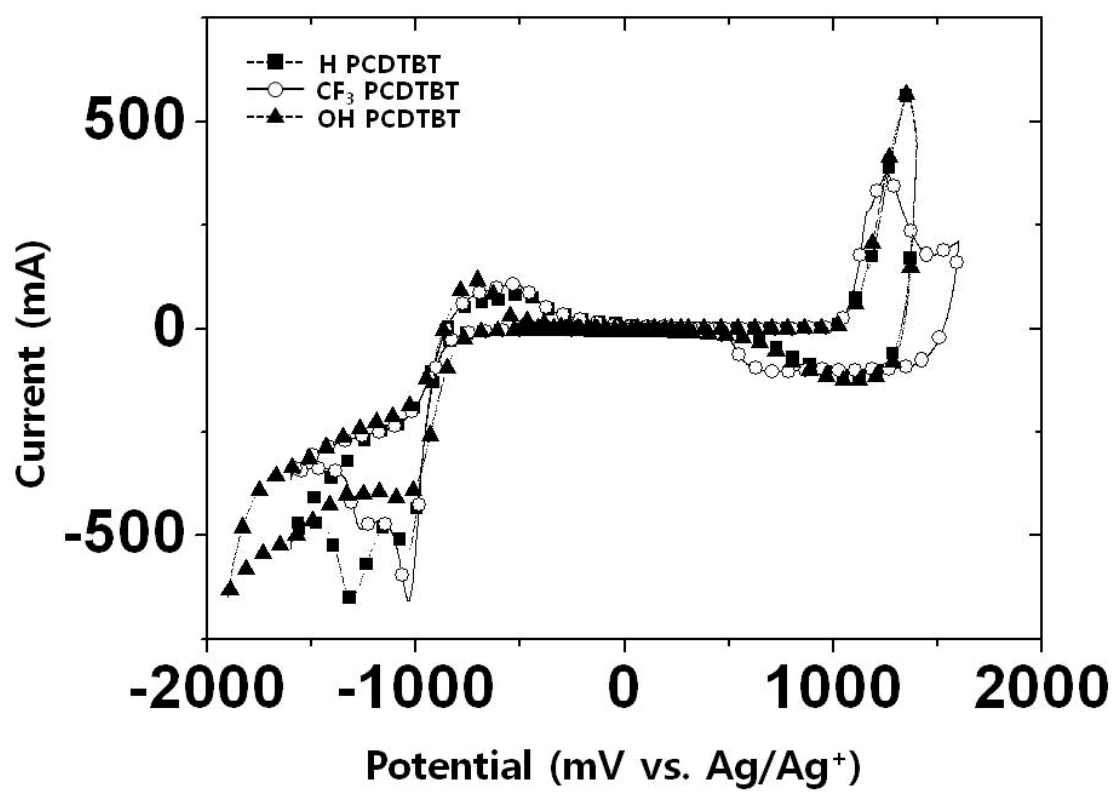


Figure S2. The cyclic voltammetry data

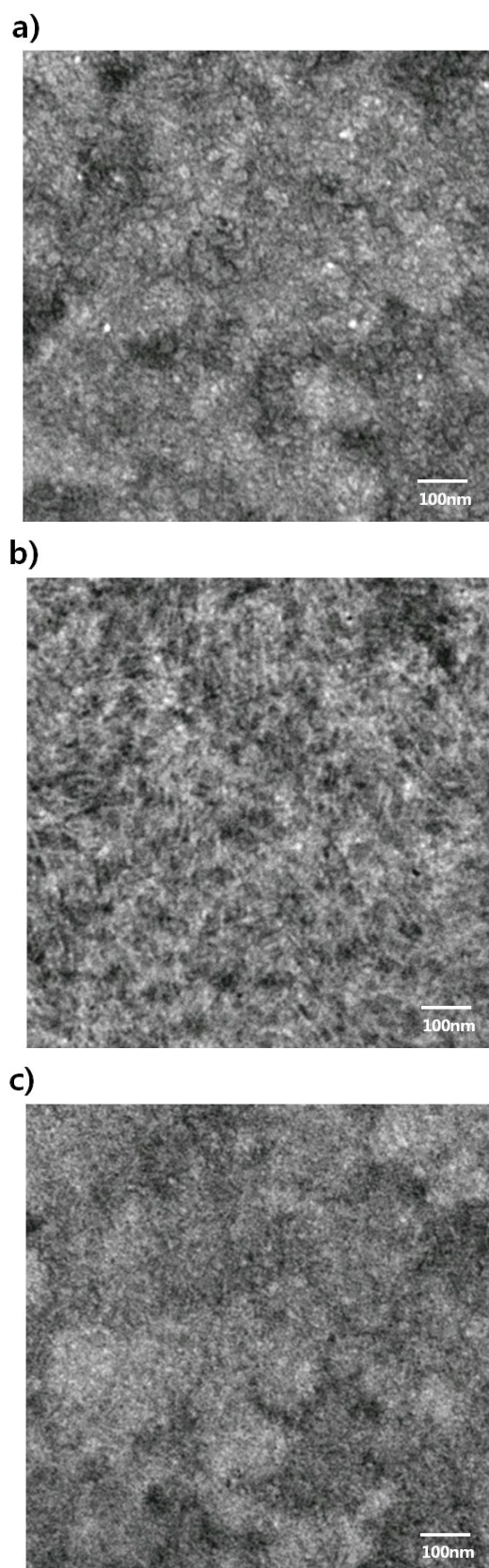


Figure S3. TEM images of the end group functionalized PCDTBT film morphology, a) H-PCDTBT, b) CF_3 -PCDTBT, c) OH-PCDTBT

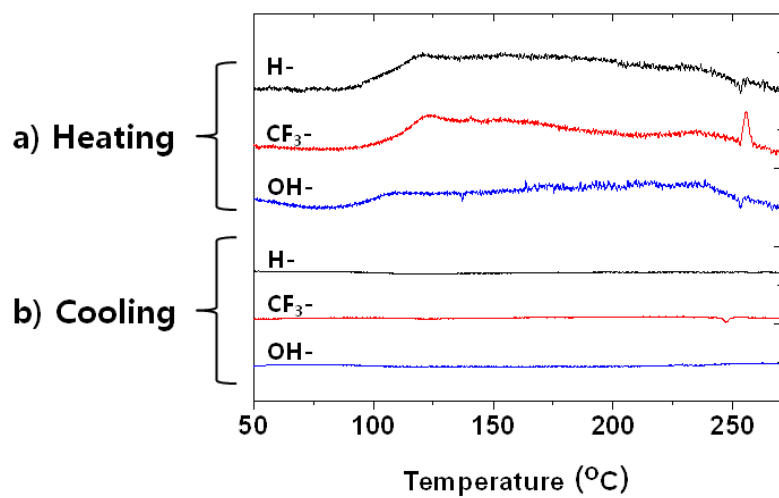


Figure S4. DSC patterns of the end-group functionalized PCDTBT

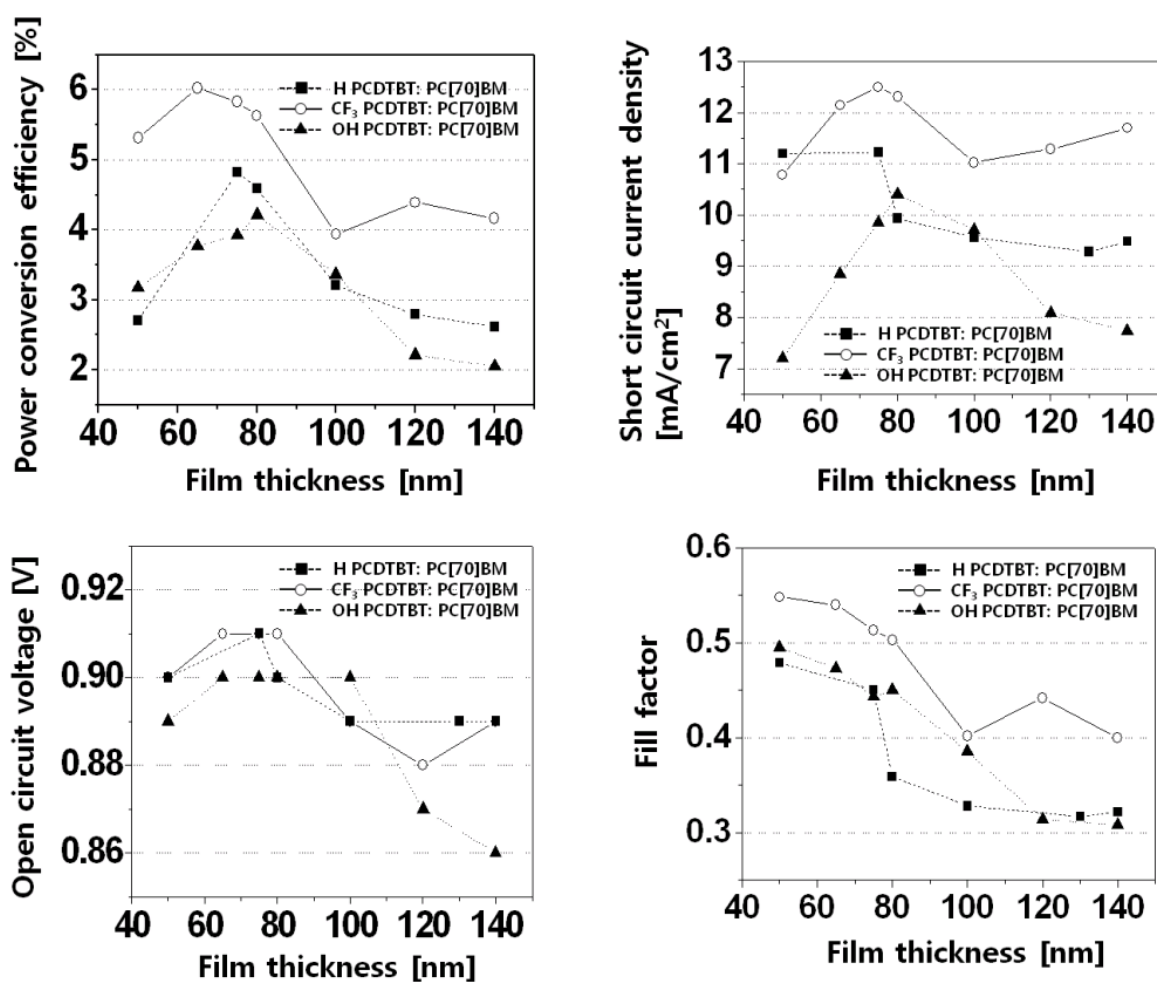


Figure S5. Device optimization by thickness of the film