

Supporting Information

Di(1-benzothieno)[3,2-*b*:2',3'-*d*]pyrrole and Isoindigo-based Electron Donating Conjugated Polymer for Efficient Organic Photovoltaics

In Hwan Jung,^{a,b*} Ji-Hoon Kim,^c So Youn Nam,^a Changjin Lee,^{a,b} Do-Hoon Hwang,^{c*} Sung Cheol Yoon^{a,b*}

^a *Advanced Materials Division, Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Republic of Korea*

^b *Chemical Convergence Materials, University of Science and Technology (UST), Daejeon 305-350, Republic of Korea*

^c *Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea*

Synthesis of the polymer

poly[(11-(2-hexyldecyl)-di(1-benzothieno)[3,2-b:2',3'-d]pyrrole-3,8-diyl)-alt-((E)-1,1'-bis(2-ethylhexyl)-isoindigo-6,6'-diyl)] (PDBTPI)

A mixture of 11-(2-hexyldecyl)-3,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-di(1-benzothieno)[3,2-b:2',3'-d]pyrrole (0.1743 g, 0.23 mmol), (E)-1,1'-bis(2-ethylhexyl)-6,6'-dibromoisindigo (0.1486g, 0.23 mmol), P(o-tol)₃ (0.12 eq, 8mg) and Pd₂(dba)₃ (0.03 eq, 6mg), was dissolved in degassed toluene (10 ml) with Aliquat® 336 (2 drops). When the temperature reached 90 °C, degassed aqueous 2M K₃PO₄ (4 ml) was added to the solution. After 24 hours, the end-capping bromobenzene (0.1 eq) in toluene (1 ml) was added. After a further 6 hours, phenyl boronic acid (0.2 eq) in toluene (1 ml) was added. The mixture was poured into methanol and the precipitate was dissolved in chloroform and filtered through Celite to remove the metal catalyst. The polymer fibers were washed by Soxhlet extraction with methanol, acetone, hexanes and chloroform. The final blue polymer was obtained after reprecipitation with methanol. (0.181 g, 79%) ¹H NMR (400MHz, CDCl₃): 9.17 (br, 4H), 7.68 (br, 4H), 7.05 (br, 2H), 6.76 (br, 2H), 3.75 (br, 6H), 2.04 (br, 3H), 1.46-1.21 (br, 40H), 0.86 (br, 18H)

Measurements: ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ascend™-400 spectrometer, with tetramethylsilane as an internal reference. The absorption spectra were measured on a SHIMADZU/UV-2550 model UV-visible spectrophotometer. Photoluminescence spectra were obtained from the Perkin Eimer/LS55 Fluorescence spectrometer. Thermogravimetric analysis (TGA) was carried out on a Thermo plus EVO II TG 8120 under a N₂ atmosphere with a heating and cooling rate of 10 °C min⁻¹. Cyclic voltammetry was performed on a BAS 100B/W electrochemical analyzer with a three-electrode cell in a 0.1 N Bu₄NBF₄ solution in acetonitrile at a scan rate of 50 mV/s. The polymer film was coated onto a Pt wire electrode by dipping the electrode into a polymer

solution in chloroform. All measurements were calibrated against an internal standard of ferrocene (Fc), the ionization potential (IP) value of which is -4.8 eV for the Fc/Fc⁺ redox system. The number- and weight-average molecular weights of the polymers were determined by gel-permeation chromatography (GPC) with a Waters 2690 Associates liquid chromatography instrument equipped with a Waters 2414 differential refractometer. Chloroform was used as the eluent and polystyrene as the standard. The morphology of the polymer:PC₇₁BM blend films was measured by transmission electron microscope (TEM) analysis (TECNAI G2 instrument)

Ultraviolet photoelectron spectroscopy (UPS): A set of samples were analyzed using the AXIS Ultra DLD model (KRATOS inc.) in Korea Basic Science Institute (KBSI), Daejeon. The He I (21.2 eV) emission line was employed as a UV source. The helium pressure in the analysis chamber during analysis was about 4.0×10^{-8} Torr. The HOMO energy level were determined using the incident photon energy, $h\nu = 21.2$ eV, E_{cutoff} , and E_{onset} .

Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) Experiments: Grazing incidence X-ray diffraction measurements were performed in vacuum at the 3C beamline in the Pohang Light Source, Korea. To make the results comparable to those of OPV devices, the samples for the measurements were prepared on PEDOT:PSS modified Si substrates under the same conditions as those used for the fabrication of solar cell devices. (i.e., the angle between the critical angle of the sample and that of Si) was 0.13°. The 2D-GIXD patterns were recorded using a 2D CCD detector (Rayonix SX165), and the X-ray irradiation time was set at 0.5–10 s, depending on the saturation level of the detector. The 2D-GIXD images from the films were analyzed based on the relationship between the scattering vector (q) and the d spacing, ($q = 2\pi/d$).

Fabrication of Photovoltaic Devices : The devices were fabricated with the following structure: ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al. The procedure for cleaning the ITO surface included sonication and rinsing in distilled water, methanol, and acetone. The hole-transporting PEDOT:PSS layer (45 nm) was spin-coated onto each ITO anode from a solution purchased from Heraeus (Clevios™ P VP AI4083). Each polymer:PC₇₁BM solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution used for spin-coating was prepared by dissolving the polymer (10 mg/mL) in chlorobenzene/1,8-diodooctane (DIO) (97:3). Calcium and aluminum contacts were formed sequentially by vacuum deposition at $< 3 \times 10^{-6}$ Torr, to provide an active area of 0.09 cm². The thickness of the active layer was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm. The current density-voltage (*J-V*) characteristics of all photovoltaic cells were determined by illuminating the cells with simulated solar light (AM 1.5 G) with an intensity of 100 mW/cm² using an Oriel 1000 W solar simulator. Electronic data were recorded using a Keithley 236 source-measure unit, and all characterizations were carried out in an ambient environment. The illumination intensity was calibrated by employing a standard Si photodiode detector (PV measurements Inc.), which was calibrated at the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was measured as a function of wavelength between 360 and 800 nm using a halogen lamp as the light source, and the calibration was carried out using a silicon reference photodiode. Measurements were carried out after masking all but the active cell area of the fabricated device. All characterization steps were carried out in an ambient laboratory atmosphere.

Table S1. Molecular, Optical and Electrochemical Properties of Synthesized Polymers

Polymer	M_n (g/mol) ^[a]	PDI	$\lambda_{\max, \text{abs}}$	$\lambda_{\max, \text{emi}}$	λ_{\max}	λ_{edge}	$\lambda_{\max, \text{emi}}$	Optical E_g^{opt} (eV) ^[c]	$E_{\text{HOMO, CV}}$	$E_{\text{HOMO, UPS}}$	$E_{\text{HOMO, DFT}}$
			(nm)	(nm)	(nm)	(nm)	(nm)		(eV)	(eV)	(eV)
			Solution	Solution	Film ^[b]	Film ^[b]	Film ^[b]				
PDBTPI	33,000	2.24	376, 602	720	376, 605	738	736	1.68	-5.24	-5.02	-4.99

^[a] M_n and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl_3 . ^[b] Polymer film on a quartz plate by spin-casting from chloroform solution at 1500 rpm for 30 s. ^[c] Calculated from the absorption band edge of the copolymer films, $E_g = 1240/\lambda_{\text{edge}}$.

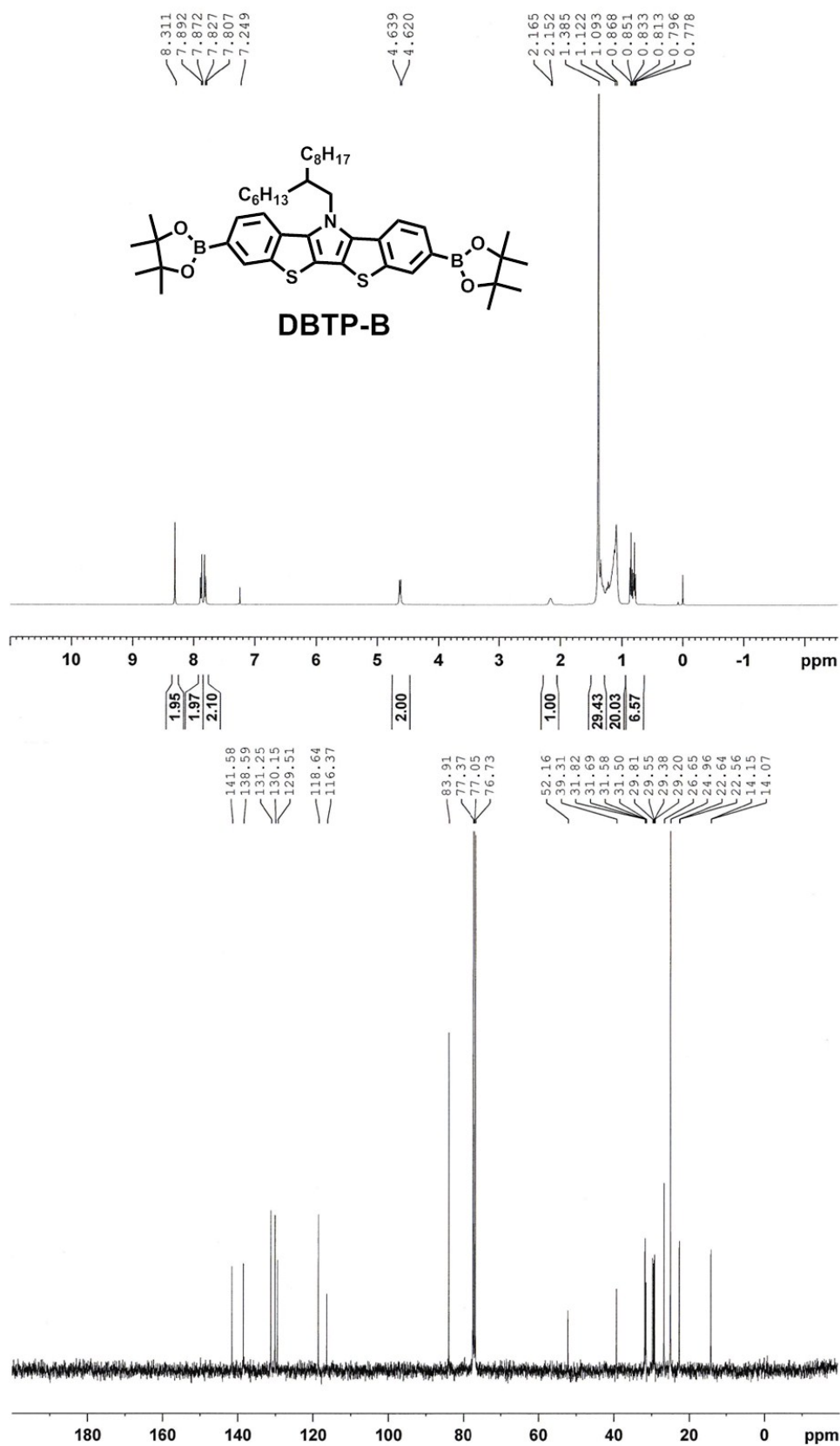


Figure S1. ¹H and ¹³C NMR spectra of 11-(2-hexyldecyl)-3,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-di(1-benzothieno)[3,2-b:2',3'-d]pyrrole (**DBTP-B**)

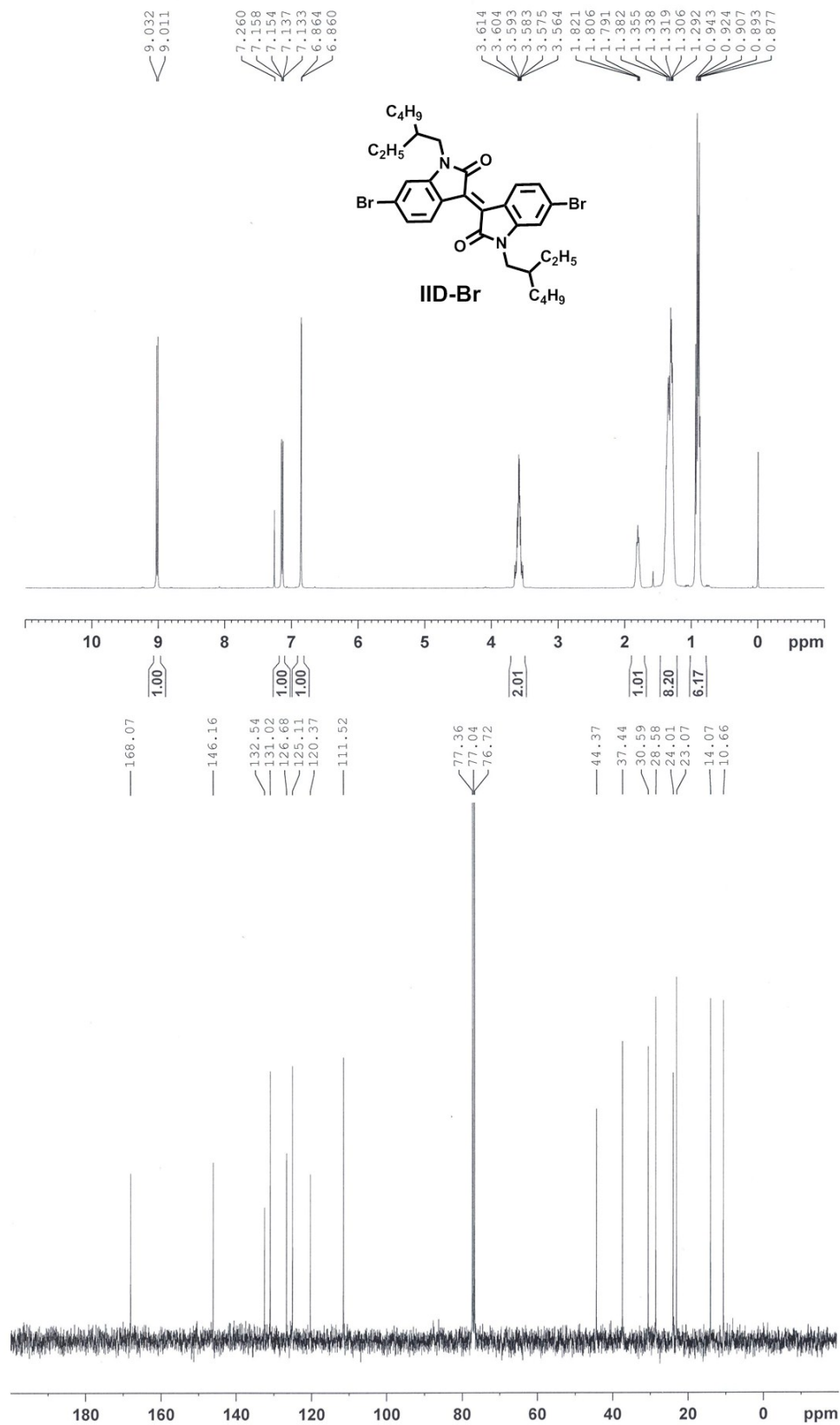


Figure S2. ¹H and ¹³C NMR spectra of (*E*)-1,1'-bis(2-ethylhexyl)-6,6'-dibromoisoidigo (IID-Br)

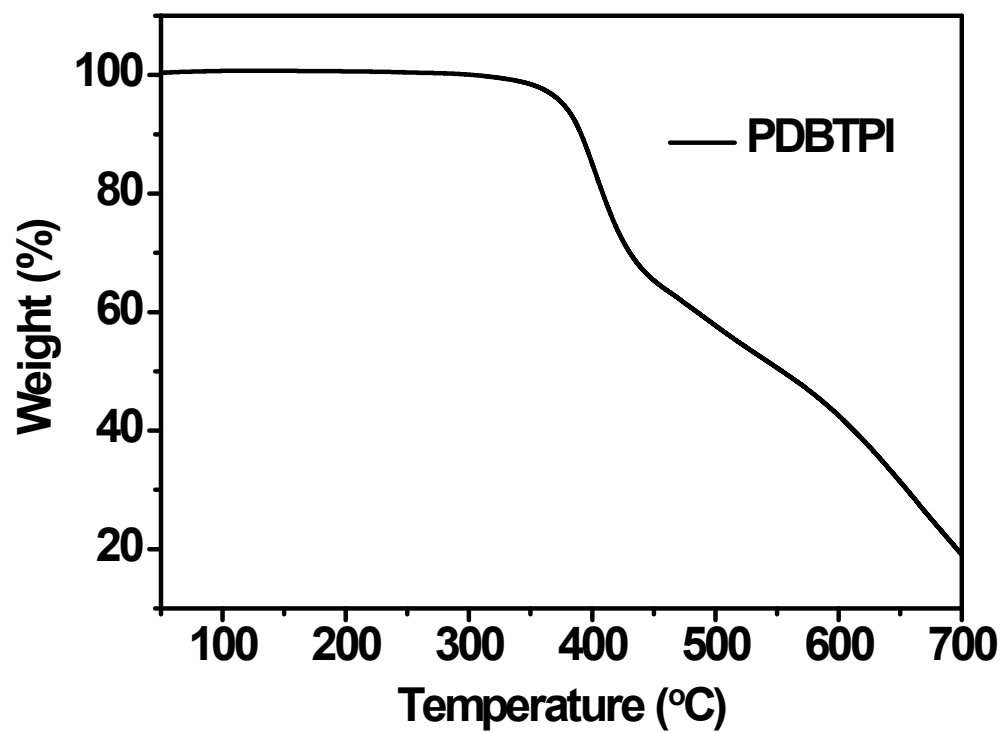


Figure S3. TGA thermogram of PDBTPI

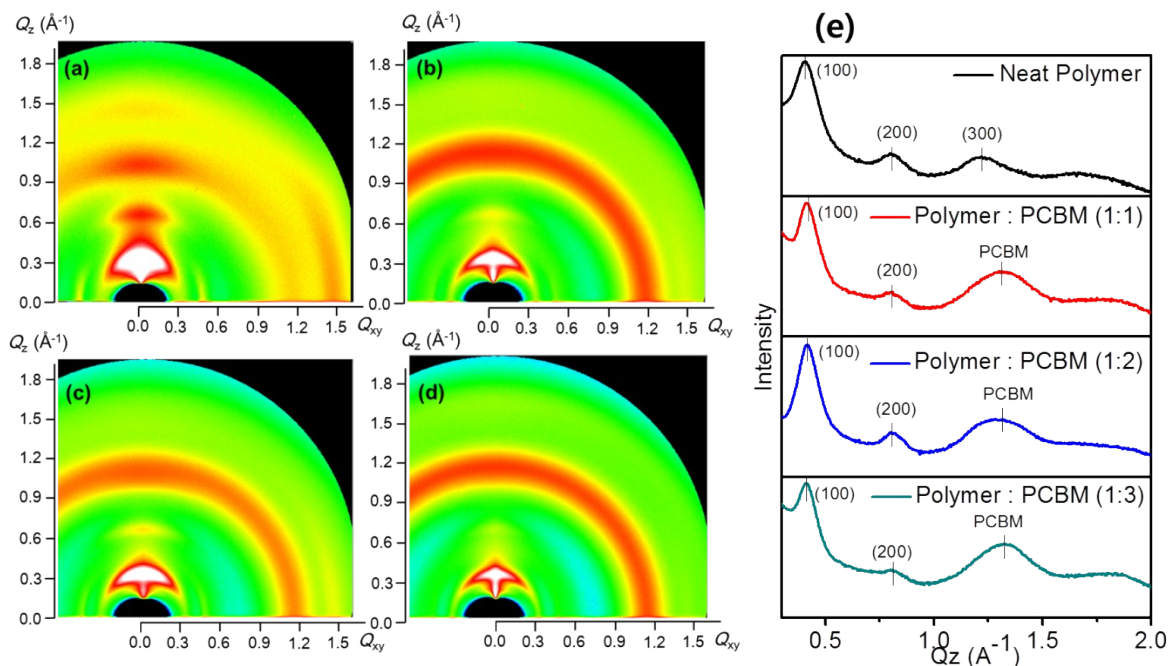


Figure S4. Two-dimensional grazing-incidence X-ray diffraction (2D-GIXD) image of neat (a) PDBTPI, and (b) PDBTPI:PC₇₁BM (1:1, w/w, with DIO), (c) (1:2, w/w, with DIO) and (d) (1:3, w/w, with DIO). (e) Out-of-plane line cuts of neat polymer and polymer:PC₇₁BM blend films.

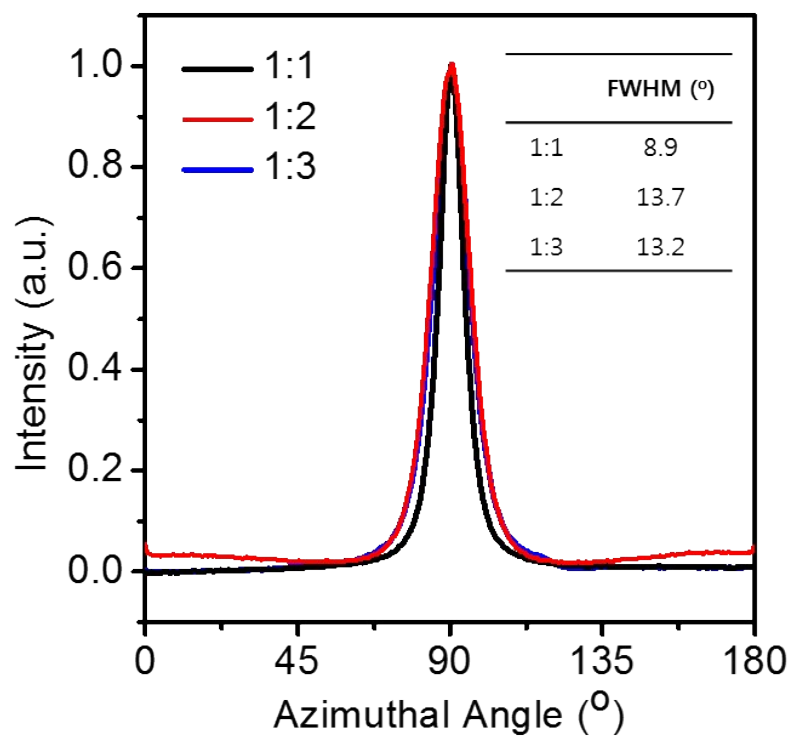


Figure S5. Azimuthal angle scans of (a) **PDBTPI:PC₇₁BM** (1:1, w/w, with DIO), (b) (1:2, w/w, with DIO) and (c) (1:3, w/w, with DIO) at $Q_{(100)}$.