Electronic Supplementary Information

Nematic Liquid Crystal Material as Morphology Regulator for Ternary Small Molecule Solar Cells with Power Conversion Efficiency Exceeding 10%

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Experimental section

The patterned indium tin oxide (ITO) substrates with a sheet resistance of 15 Ω sq^{-1} were pre-cleaned by sequential ultrasonic treatment in detergent, deionized water and ethanol, respectively. The cleaned ITO substrates were further dried by high purity nitrogen and treated by oxygen plasma for 1 min to improve its work function and clearance. Poly(3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS, clevios PVP Al 4083, purchased from H.C. Starck Co., Ltd.) solution was then spin-coated on the ITO substrates at 5000 RPM for 40 s and baked at 120℃ for 15 min in air. The small molecules of DRCN5T and BTR were purchased from 1-material Inc. and fullerene derivative $PC_{71}BM$ was purchased from Solarmer Materials Inc. The conjugated polyelectrolyte poly [(9,9-bis(3-(N,N-dimethylamino)-propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN) purchased from Organtec Materials Inc. All these materials were used as received. The DRCN5T:$PC_{71}BM$ and BTR:$PC_{71}BM$ with 1:0.8 weight ratio were dissolved in $CHCl_3$ to prepare 18 mg/mL binary blend solutions, respectively. After heated and stirred at 40℃ for 12 h, the binary blend solutions were mixed by different volume ratios to obtain ternary blend solutions of $DRCN5T_{1-x}$:BTR_x:$PC_{71}BM_{0.8}$ (x=0, 0.5, 1.0, 1.5, 2.0, 5.0 wt%, x represents BTR amount in donors). PFN was dissolved in methanol with addition of 0.25 vol% acetic acid to prepare 0.2 mg/mL solution. All blend solutions were continuously heated and stirred at 40℃ for at least 12 h before spin-coating the active layers. Subsequently, the prepared binary or ternary blend solutions were spin-coated on PEDOT:PSS modified ITO substrates at 1200 RPM for 40 s in high-purity nitrogen-filled glove box. The prepared active layers were suffered from different post-treatments: i) thermal annealing at 120℃ for 10 min with active layer upward (TA), ii) thermal annealing at 120℃ for 10 min with active layer up-side-down (DTA), iii) $CHCl_3$ solvent vapor annealing with active layer up-side-down (DSVA). Afterwards, a PFN cathode interlayer was spin-coated onto active layers at 3000 RPM for 40

s. Finally, 100 nm Al was deposited by thermal evaporation with a shadow mask. The effective area of cell is ~3.8 mm^2, which is defined by the vertical overlap of ITO and Al electrodes.

The current-voltage (*I-V*) curves of the SMSCs were measured in dark and under light illumination using a Keithley 2400 source meter in high-purity nitrogen-filled glove box. The AM 1.5G illumination was provided by a XES-40S2-CE (SAN-EI Electric Co., Ltd.) solar simulator (AAA class, 40×40 mm^2 effective irradiated area) with light intensity of 100 mW/cm^2. The light intensity was determined by standard silicon solar cells purchased from Zolix INSTRUMENTS CO., LTD. calibrated by National Institute of Metrology, China. The EQE spectra of the SMSCs were measured by a Zolix Solar Cell Scan 100. The thickness of both binary and ternary blend films was ~120 nm measured by an Ambios Technology XP -2 stylus Profiler. The absorption spectra of films were obtained by a Shimadzu UV-3101PC spectrometer. The PL spectra of films were measured by a HORIBA Fluorologs-3 spectrofluorometer system. The TRPL spectra were measured by using a FluoroCube-01-NL purchased from HORIBA Jobin Yvon. The excitation light for TRTPL was provided by a NanoLED-460 (HORIBA Scientific). The pulse width of NanoLED-460 is <1.3 ns and the typical power is 7 pJ/pulse. The fluorescence lifetime was calculated by DAS6 decay analysis software with Foundation Pack (including 1 to 5 exponentials) and DAS6-8 Anisotropy. The fluorescence lifetime can be obtained according to $I(t) = I_0 exp(-t/\tau)$, where, $I(t)$ is the fluorescence intensity at time *t,* I_0 is the fluorescence intensity at time *t=0*, τ is the fluorescence lifetime. As the complexity and diversity of actual sample, the lifetime generally be given by multi exponential decay equation, $I(t) = \sum_i a_i exp\left(-\frac{t}{\tau_i}\right)$, where $a_i$is pre-exponential factor of item *i*. In order to remove the effect of instrument response on the measurement results, colloidal SiO_2 astigmatism (Ludox) was used as a virtual sample for the

calibration. In this work, the fluorescence lifetime was the averaged lifetime obtained from a three-exponential fit. The decay model is given by: $F(t) = A + B_1 exp\left(\frac{-t}{\tau_1}\right) + B_2 exp\left(\frac{-t}{\tau_2}\right) + B_3 exp\left(\frac{-t}{\tau_3}\right)$, A is value for the background and B are the values for amplitude fit parameters. For a good fit χ^2 value should be near to 1.0 (<1.2 is usually ok provided the residuals are random). The XPS and UPS data were measured by an ultrahigh vacuum system (10^{-9} Pa) with a hemispherical electron analyzer, a twin anode X-ray gun, and a He discharge lamp. The GIXD data were obtained at 1W1A, Beijing Synchrotron Radiation Facility (BSRF). A bent-triangle silicon crystal was used to select the X-rays of a 1.5476 Å wavelength and an optimal grazing angle of 0.4° was selected to maximum the diffraction peak intensity from the samples. The TEM images were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV.

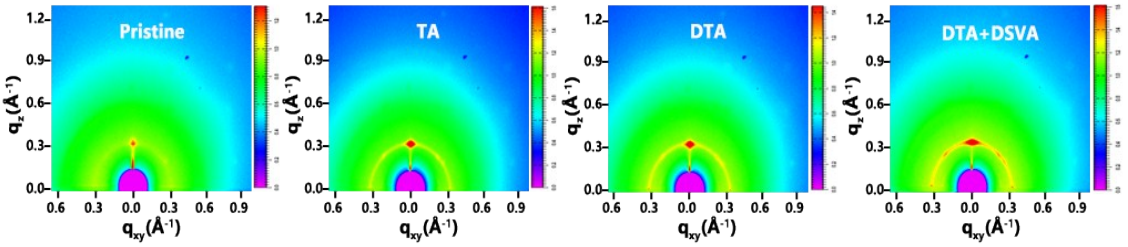

Fig. S1 2D-GIXD patterns of binary blend films with different post-treatments.

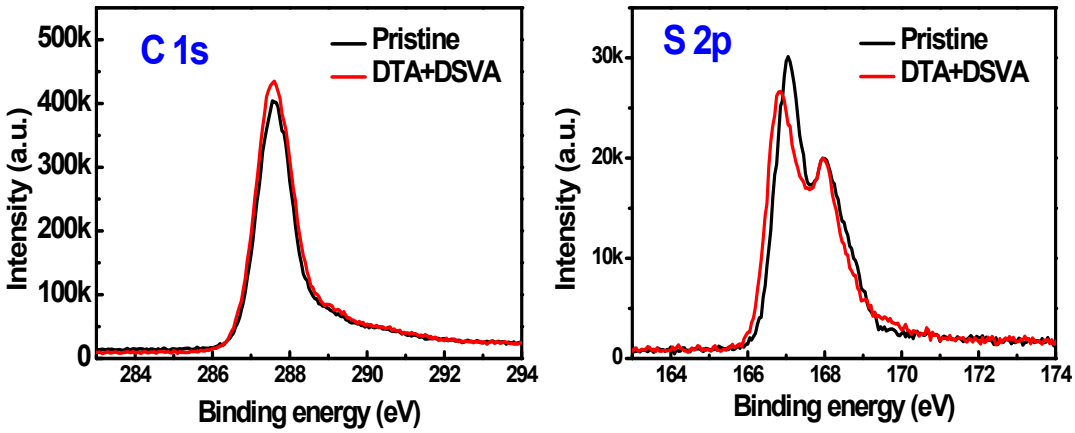

Fig. S2 The XPS of the DRCN5T:$PC_{71}BM$ blend films without any treatment or with DTA and DSVA treatments.

Calculation of the surface compositions

The mole number ratio of $PC_{71}BM$ ($C_{82}H_{14}O_2$) to DRCN5T ($C_{70}H_{86}N_6S_7O_2$) can be calculated by using the following formula:

$$\frac{n_C}{n_S} = \frac{82 \times n_{PC_{71}BM} + 70 \times n_{DRCN5T}}{7 \times n_{DRCN5T}} \quad (1)$$

Where, $n_{PC_{71}BM}$ and n_{DRCN5T} are mole number of $PC_{71}BM$ and DRCN5T. The weight ratio of $PC_{71}BM$ to DRCN5T can be determined by using the following formula:

$$\frac{W_{PC_{71}BM}}{W_{DRCN5T}} = \frac{n_{PC_{71}BM} \times M_{PC_{71}BM}}{n_{DRCN5T} \times M_{DRCN5T}} \quad (2)$$

Where, $M_{PC_{71}BM}$ and M_{DRCN5T} are the molar mass of $PC_{71}BM$ and DRCN5T.

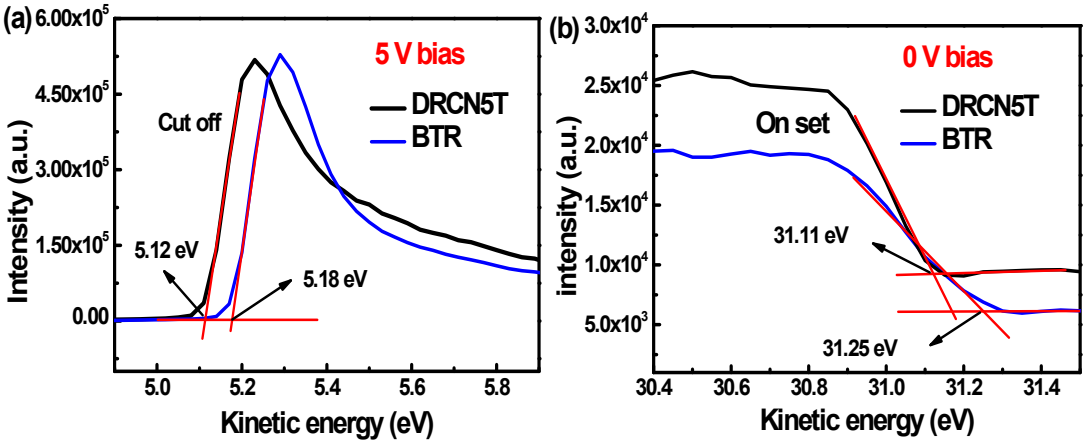

Fig. S3 The UPS spectra of neat DRCN5T and BTR films spin-coated on ITO substrates.

Table S1 The energy parameters of DRCN5T and BTR, abstracted from the UPS spectra of neat DRCN5T and BTR films.

Materials	*hv* [eV]	E_{cutoff} [eV]	E_{oneset} [eV]	E_{HOMO} [eV]	E_{LUMO} [eV]
DRCN5T	36.31	5.12	31.11	5.32	3.77
BTR	36.45	5.18	31.25	5.38	3.61

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测 试 报 告
Test Report

证书编号 GXtc2016-2085
Certificate No.

客户名称 Client	北京交通大学发光与光信息教育部重点实验室 Key Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing Jiaotong University
器具名称 Instrument	三元小分子有机太阳能电池 Ternary Small Molecule-Based Organic Solar Cell
型号/规格 Type/Model	DRCN5T:BTR:$PC_{71}BM$
出厂编号 Serial No.	7#-1
生产厂家 Manufacturer	张福俊教授课题组 Professor Zhang Fujun Research Group
客户地址 Address	北京市海淀区上园村 3 号
测试日期 Date of Test	2016-11-29

批准人： Approved by

中国计量科学研究院 测试专用章

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证书编号 GXtc2016-2085
Certificate No.

中国计量科学研究院是国家最高的计量科学研究中心和国家级法定计量技术机构。1999 年授权签署了国际计量委员会（CIPM）《国家计量基(标)准和国家计量院签发的校准与测量证书互认协议》（CIPM MRA）。The National Institute of Metrology (NIM) is China's national metrology institute (NMI) and a state-level legal metrology institute. NIM is China's signatory to the Mutual Recognition of National Measurement Standards and of Calibration and Measurement Certificates Issued by National Metrology Institutes (CIPM MRA) which is arranged by the International Committee of Weights and Measures (CIPM).
中国计量科学研究院的质量管理体系符合 ISO/IEC17025 标准，通过中国合格评定国家认可委员会和亚太计量规划组织（APMP）联合评审的校准和测量能力（CMCs）在国际计量局（BIPM）关键比对数据库中公布。NIM's quality management system meets requirements of the ISO/IEC 17025. Its Calibration and Measurement Capabilities (CMCs) that are peer reviewed both by China National Accreditation Service for Conformity Assessment (CNAS) and the Asia Pacific Metrology Programme (APMP) are published in the International Bureau of Weights and Measures (BIPM) Key Comparison Database (KCDB).
2011 年，中国计量科学研究院和中国合格评定国家认可委员会就认可领域的技术评价活动签署了谅解备忘录，承认中国计量科学研究院的计量支撑作用和出具的校准/检测结果的溯源效力。NIM and CNAS signed a Memorandum of Understanding (MOU) for Recognition of Technical Assessment in Laboratory Accreditation Field in 2011, in which CNAS recognizing the technical supporting role of NIM in laboratory accreditation and the traceability of NIM's calibration / test results.
测试结果不确定度的评估和表述均符合 JJF1059 系列标准的要求。The evaluation and expression of uncertainty of the test results are in line with the requirements of JJF1059 series standards.

测试所依据的技术文件（代号、名称）Reference documents (Code,Name)
Measurement of photovoltaic current-voltage characteristics（IEC60904-1）
太阳电池测试规范：光电性能（NIM-ZY-GX-TT-402）(Test Specification of Solar Cells: Photoelectric Properties)

测试环境条件及地点 Test place and environment
温 度 Temperature：25 ℃ 地 点 Location： 光学楼 110 室
湿 度 Humidity：45 % RH 其 它 Others：

测试使用的计量基（标）准装置(含标准物质)/主要仪器
Reference Standards（Including the Reference Material）/ Instruments used

名 称 Name	测量范围 Measurement Range	不确定度/准确度等级 Uncertainty/Accuracy	证书编号 Certificate No.	证书有效期至 Due Date (YYYY-MM-DD)
太阳电池光电性能校准装置 Measurement Standard	I_{sc}:（0.1-10）A V_{oc}: (0.1-200)V P_m:(0.01-500) W	I_{sc}: 1.5%（k=2） V_{oc}: 0.5% (k=2) P_m:1.6% (k=2)	[2015]国量标计证字第 286 号	2019-07-05
KG5-标准太阳电池 KG5-Reference solar cell	I_{sc}:（0-200）mA	1.2% (k=2)	GXtc2016-0080	2017-02-26

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证书编号 GXtc2016-2085
Certificate No.

测 试 结 果
Calibration Results

1. **测试条件 Test Conditions:**
标准太阳电池：KG5-单晶硅；
Reference Solar Cell: KG5 filterd mono-Si;
标准太阳电池的标定值：38.9 mA；
CV of Reference Solar Cell：38.9 mA；
太阳模拟器等级：AAA 级；
Solar Simulator Classification：AAA 级；
温度传感器/控制系统：无。
Teperature Sensor/Control System: None。
扫描方向：反扫
Scan Direction: reverse

2. **I-V 特性参数 I-V Characteristic parameters:**
以上述标准太阳电池标定太阳模拟器辐照度至 1000 W/m^2，校准被测太阳电池的 I-V 特性曲线和参数如下：
By using the above reference solar cell to calibrate the solar simulator's irradiance to 1000 W/m^2, the I-V characterisitc curve and parameters as follows:

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Certificate No.

测 试 结 果
Calibration Results

有效面积（mm^2）	短路电流 I_{sc}(mA)	开路电压 V_{oc}(V)	最大功率 P_{max}(mW)
3.84	0.58	0.92	0.36

最大功率电流 I_{max}(mA)	最大功率电压 V_{max}(V)	填充因子 FF (%)	转换效率 (PCE) η (%)
0.49	0.74	67.5	9.38

注 Note:
1. 太阳电池的有效面积为 3.84mm^2（证书编号：CDjc2016-8282）。
The certificated cell area is 3.84mm^2 (Certificate No.: CDjc2016-8282).
2. 此数据仅对被测样品当时状态有效。
The data apply only at the time of the test for the sample.
备注：
器件在空气中测试且无封装
The device was tested in air without encapsulation.

建议 Suggestion:
根据客户要求和测试文件的规定，通常情况下 12 个月校准一次。
According to the client or the test documents, the recommended calibration cycle is 12 months.

声明 Statement:
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NIM is ONLY responsible for the complete certificate with the calibration stamp of NIM.
2.本证书的测试结果仅对所校准的计量器具有效。
The certificate is ONLY valid for the test ed instrument.
3.本证书用中英文两种语言表达，准确含义以中文为准。
The certificate is reported in both English and Chinese, with the Chinese version as standard.

测 试 员： 张碧丰 核 验 员：

Fig. S4 Calibration report of PCE for the optimized DRCN5T:BTR:$PC_{71}BM$-based ternary SMSCs tested in National Institute of Metrology, China.

中国计量科学研究院

测 试 报 告

报告编号 CDjc2016-8282

客户名称 北京交通大学

样品名称 有机太阳能电池器件

型号/规格 7#DRCN5T:BTR:PC71BM

出厂编号 7#

生产厂商 /

客户地址 北京市海淀区上园村 3 号

测试日期 2016 年 11 月 30 日

批准人：

中国计量科学研究院 1 测试专用章

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中国计量科学研究院

报告编号 CDjc2016-8282

中国计量科学研究院是国家最高的计量科学研究中心和国家级法定计量技术机构。1999 年授权签署了国际计量委员会（CIPM）《国家计量基(标)准和国家计量院签发的校准与测量证书互认协议》（CIPM MRA）。

中国计量科学研究院的质量管理体系符合 ISO/IEC17025 标准，通过中国合格评定国家认可委员会和亚太计量规划组织（APMP）联合评审的校准和测量能力（CMCs）在国际计量局（BIPM）关键比对数据库中公布。

2011 年，中国计量科学研究院和中国合格评定国家认可委员会就认可领域的技术评价活动签署了谅解备忘录，承认中国计量科学研究院的计量支撑作用和出具的校准/检测结果的溯源效力。

测试所依据/参考的技术文件（代号、名称）
按用户提供技术文件要求测量

测试环境条件及地点：
温 度：20.1 ℃ 地 点： 恒温楼 1001 房间
湿 度：45 % RH 其 它： /

测试使用的计量基（标）准装置（含标准物质）/主要仪器

名 称	测量范围	不确定度/准确度等级	证书编号	证书有效期至 (YYYY-MM-DD)
影像测量仪	（400×200）mm	（1.8+L/300）μm	CDjc2015-5164	2017 年 05 月 15 日

中国计量科学研究院

报告编号 CDjc2016-8282

测 试 结 果

1. 外观轮廓：样品由用户制备提供，显微镜下图形轮廓不平直；
2. 目标图形（方形）实测面积：
   测量方块的四个角点坐标，计算其组成的封闭图形面积：

编号	有效面积 mm^2
7#	3.84
测量不确定度 k=2	0.07mm^2

以下空白

声明：
1. 我院仅对加盖“中国计量科学研究院测试专用章”的完整报告负责。
2. 本报告的测试结果仅对本次所测试的样品有效。

测 试 员： 核 验 员：

Fig. S5 Calibration report of effective area tested in National Institute of Metrology, China.

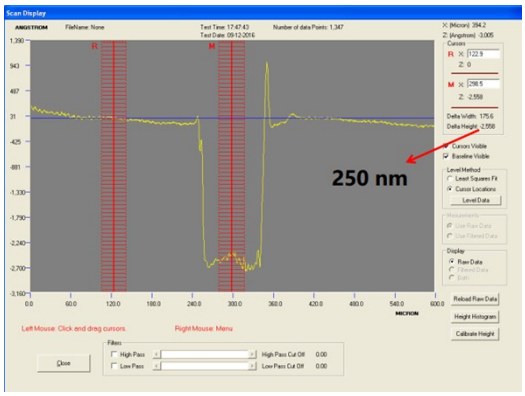

Fig. S6 The thickness of BTR:$PC_{71}BM$ blend film.

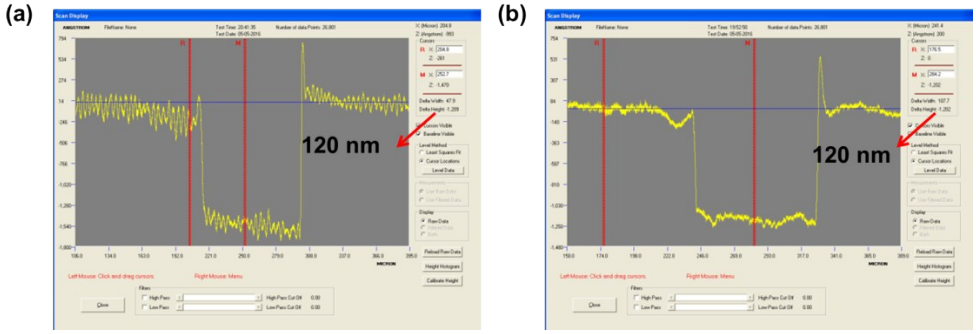

Fig. S7 The thickness of the optimized DRCN5T:$PC_{71}BM$ blend film (a), the optimized ternary blend film (b).

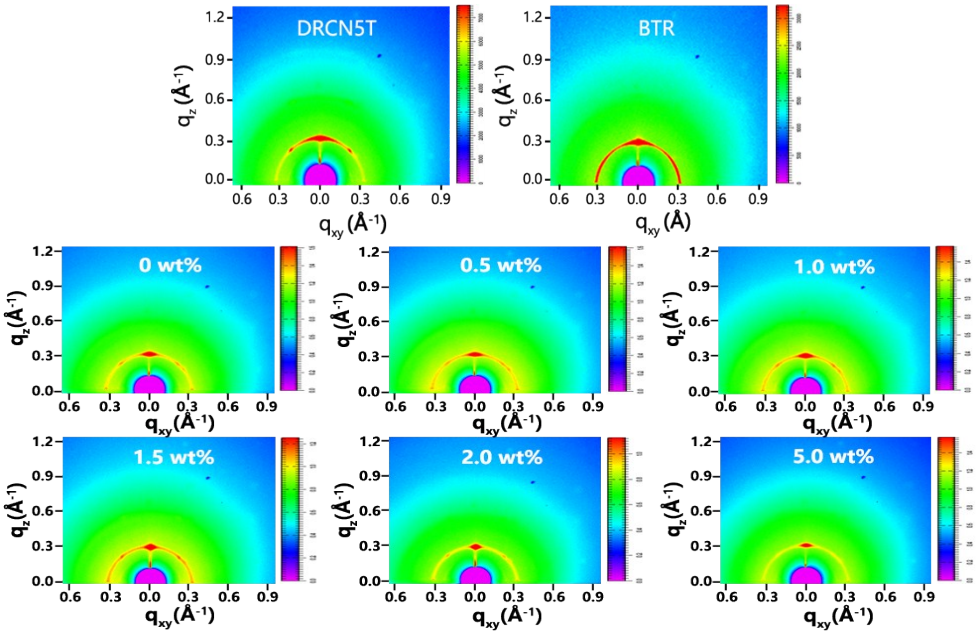

Fig. S8 2D-GIXD patterns of neat DRCN5T, BTR films and the blend films with different amount of BTR.

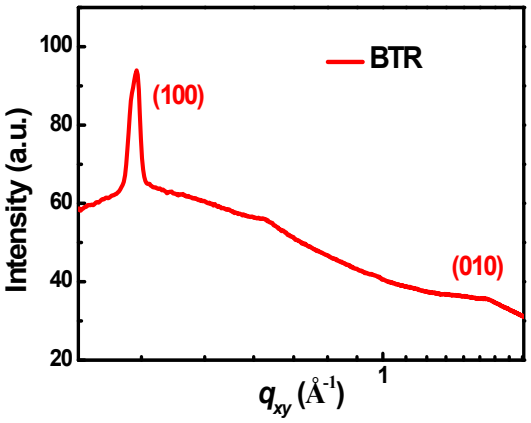

Fig. S9 The in-plane line-cut of neat BTR film.

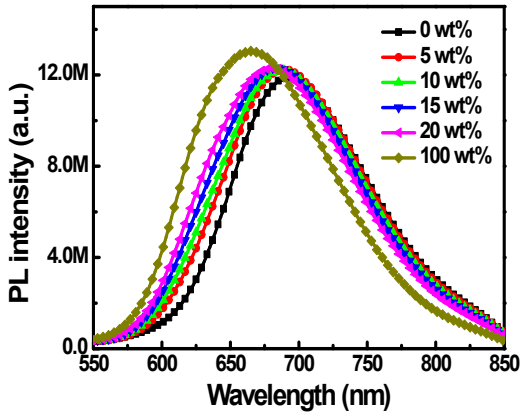

Fig. S10 PL spectra of DRCN5T:BTR blend solutions (5 mg/mL) with different amount of BTR.

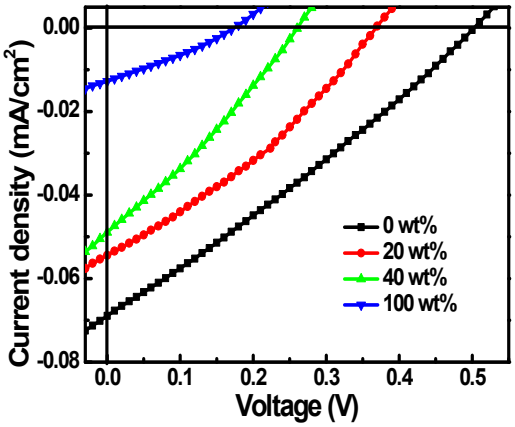

Fig. S11 *J-V* curves of cells with DRCN5T:BTR as active layers (without $PC_{71}BM$) under AM 1.5G illumination (100 mW cm^{-2}).