

## Supporting Information

### **A low bandgap n-type polymer based on fused-DAD-type heptacyclic ring for all-polymer solar cell application with a power conversion efficiency of 10.7%**

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## Experiment Section

### Instruments

UV-vis spectra were identified with a Lambda 950 spectrophotometer. Electrochemical CV was tested on an electrochemical workstation (Chenhua, Shanghai) with a Pt disk coated with a molecular film, a Pt plate, and an Ag/AgCl electrode acting as the working, counter, and reference electrodes, respectively, in a 0.1 mol L<sup>-1</sup> tetrabutylammonium phosphorus hexafluoride (Bu<sub>4</sub>NPF<sub>6</sub>) acetonitrile solution. The scan rate for the CV measurements was 100 mV s<sup>-1</sup>. The *J-V* curves were obtained in air with a Keithley 2420 source measure unit. Newport Thermal Oriel 91159 A solar simulator was used for J-V curves measurement under AM 1.5 G (100 mW cm<sup>-2</sup>). The EQE measurements of the devices were performed in air with an Oriel Newport system (Model 66902). The thickness of the active layer was measured on a Kla-Tencor Alpha-StepD-120 Stylus Profiler. Two-dimensional grazing incidence wide angle X-ray scattering (2D-GIXD) analyses were measured at the XEUSS SAXS/WAXS equipment. The data were obtained with an area Pilatus 100k detector with a resolution of 195 × 487 pixels (0.172 mm × 0.172 mm). The X-ray wavelength was 1.54 Å, and the incidence angle was 0.2°. The samples were spin-coated onto the PEDOT:PSS/Si substrate. The samples were prepared with the optimized device fabrication conditions. AFM images were obtained on a Multimode 8 in tapping mode. <sup>1</sup>H NMR (400 MHz) spectrum is obtained using a Bruker AVANCE III HD 400 with tetramethylsilane as an internal standard.

### Photovoltaic device fabrication

The OSCs devices were fabricated with a configuration of ITO/PEDOT:PSS/PBDB-T:A701 /PDINO/Al. A thin layer of PEDOT:PSS (30 nm, Clevios P Vp.AI 4083) was spin-cast on pre-cleaned ITO-coated glass at 3000 rpm. After baking at 150 °C for 20 min, the substrates were transferred into glovebox. Optimized devices were prepared under the following conditions. The Donor: Acceptor (D:A) ratio of 1:1.5 (w/w) was dissolved chloroform (CF) with a total concentration of 15 mg/mL for 1 hour at 60 °C and then the active layers was spin-coated from the above solution with a speed of 3000

rpm. The effects of solvents, additive concentrations, thermal annealing temperature, and blend ratios on device performance were also examined. The optimized thickness of the blend film is in the range 100-120 nm. Finally, a PDINO/Al (80 nm) metal top electrode was thermal evaporated onto the active layer under about  $2 \times 10^{-6}$  mbar. The active area of the device was 0.04 cm<sup>2</sup> defined by shadow mask.

### **Carrier Mobilities.**

The hole mobility of the polymer was investigated by the space charge limited current (SCLC) method. The hole only mobility of the blend films was measured with the device structure of ITO/PEDOT:PSS/active layer (~100 nm)/Au (80 nm) while the electron only mobility of the blends was measured with the device structure of ITO/TiOx/active layer(~100 nm)/Al (80 nm).

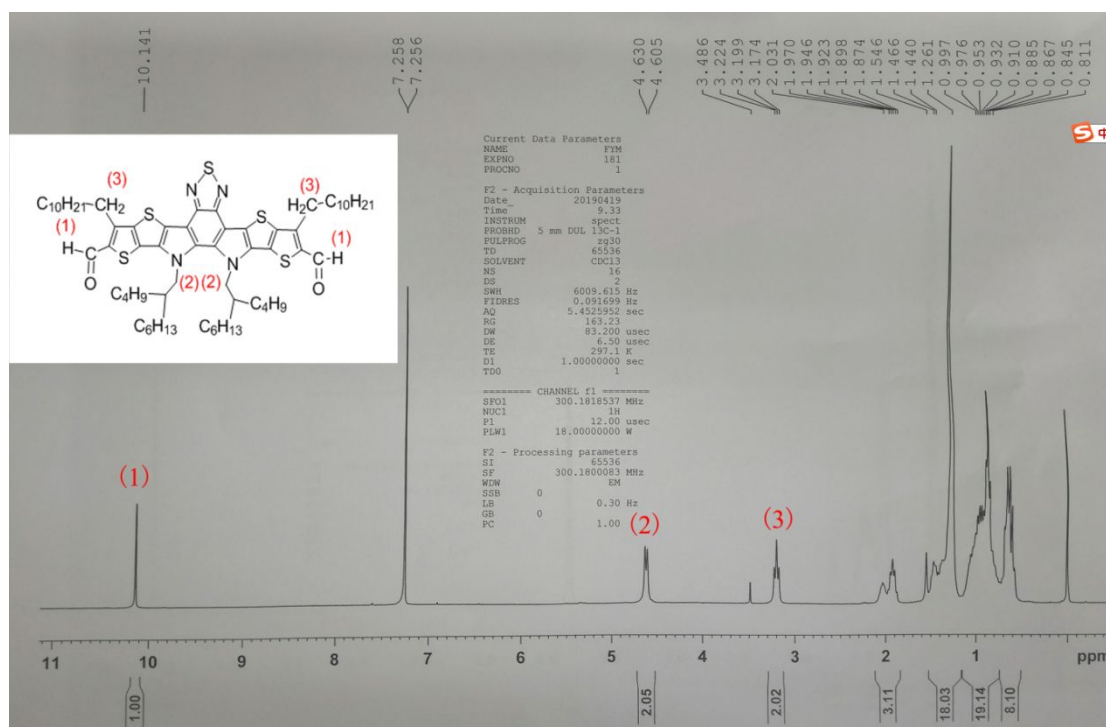
The SCLC model is described by modified Mott-Gurney law:

$$J = (9/8)\epsilon_0\epsilon_r\mu(V^2/L^3)\exp[0.89\beta(V/L)^{0.5}]$$

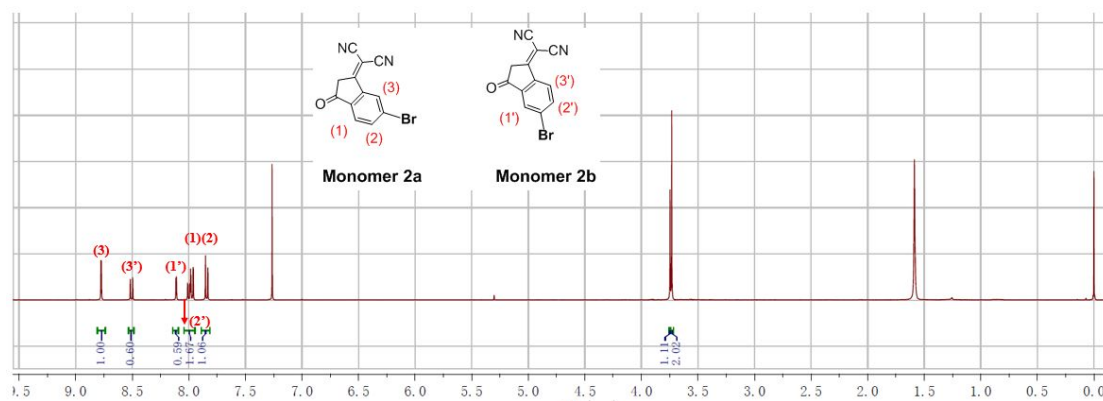
where  $J$  stands for current density,  $\epsilon_0$  is the permittivity of free space ( $8.85 \times 10^{-12} \text{CV}^{-1} \text{m}^{-1}$ ),  $\epsilon_r$  is the relative dielectric constant of the transport medium (assuming that 3.0),  $\mu$  is the carrier mobility,  $V$  is the internal potential in the device and  $L$  is the thickness of the active layer,  $\beta$  is the field activation factor.

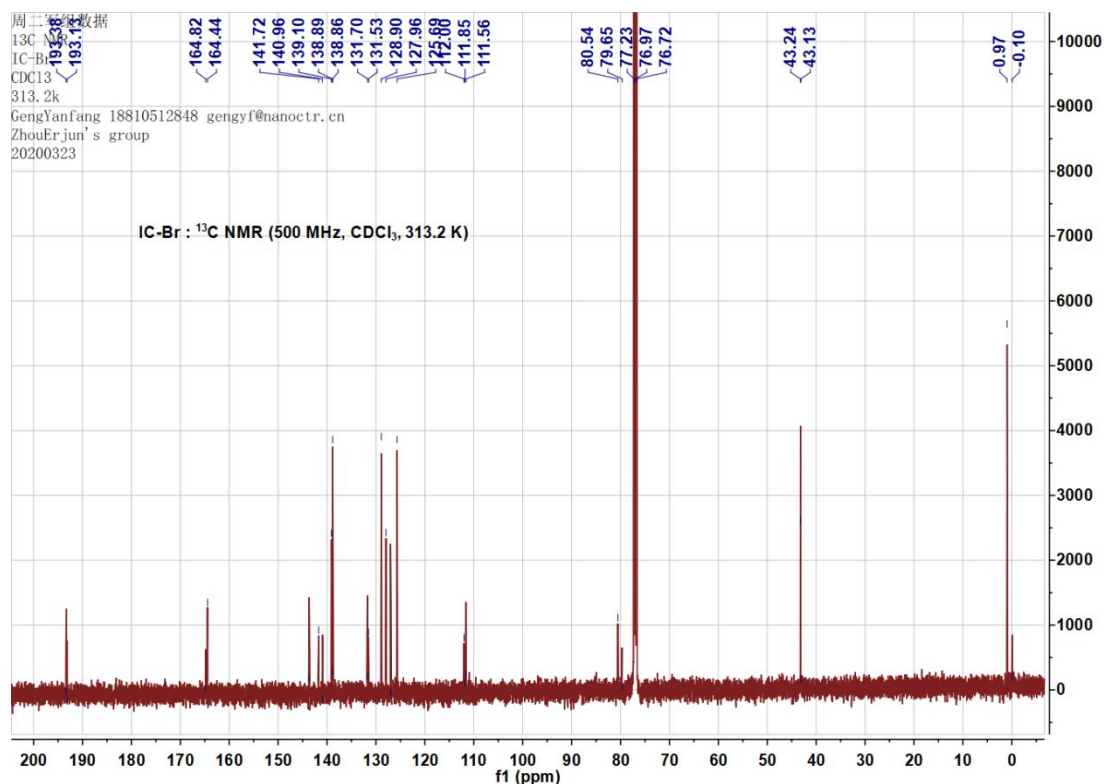
### **Materials and Synthesis:**

Compound **1** and IC-Br were synthesized by Organtec Ltd. The p-type polymer of PBDB-T was purchased from Solarmer Ltd, with Mw of 21.9 kDa and PDI of 1.81. The other chemicals and solvents were purchased from J&K, Alfa Aesar, TCI, Beijing Chemical Plant or other chemical companies and used without further purification.



**Figure S1.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, room temperature) of **monomer 1**.

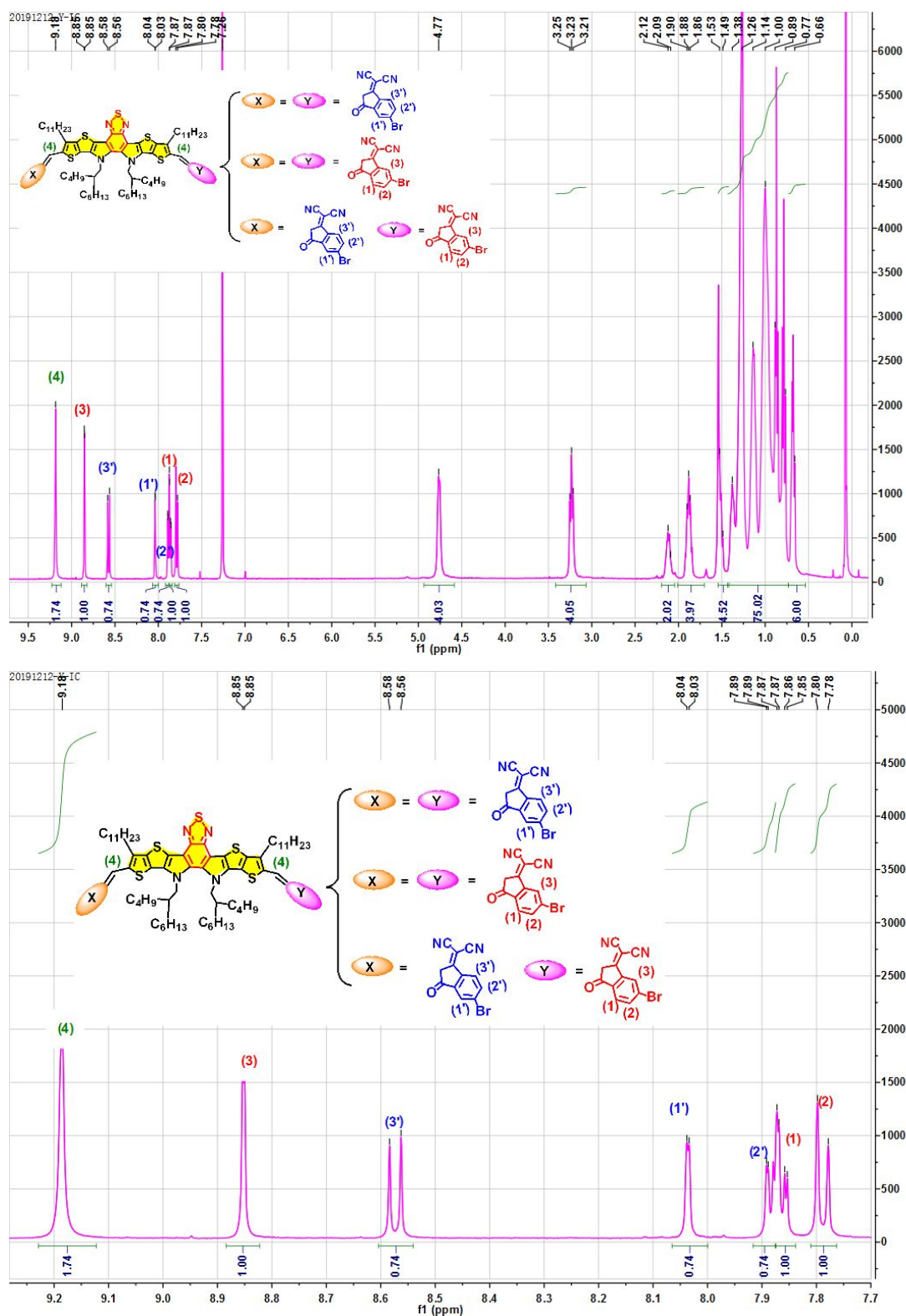




**Figure S2.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS, room temperature) of **monomer 2 (IC-Br)** and  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , TMS, 313.2K) of **monomer 2 (IC-Br)**.

### Synthesis of compound 3.

In a dry 50 mL flask, compounds 1 (0.15 g, 0.13 mmol), IC-Br (0.14 g, 0.52 mmol) and pyridine (1 mL) were added to a solution of 20 mL degassed  $\text{CHCl}_3$  under nitrogen and stirred vigorously at  $65^\circ\text{C}$  for 8 h. Then the mixture was poured into methanol (140 mL) and a precipitate was formed and collected. The resulting crude compound was purified by using silica gel to give a black solid (0.14 g, 60%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS, room temperature),  $\delta$ (ppm):  $\delta$  9.18 (s, 1.74 H), 8.85 (d, 1 H), 8.58 (d, 0.74 H), 8.04 (d, 0.74 H), 7.87 (m, 0.74 H), 7.80 (m, 1 H), 7.78 (d, 1 H), 4.77 (d, 4 H), 3.25 (t, 4 H), 2.12 (m, 2 H), 1.88 (m, 4 H), 1.49 (m, 4 H), 0.69-1.31 (m, 75 H), 0.66 (m, 6 H).

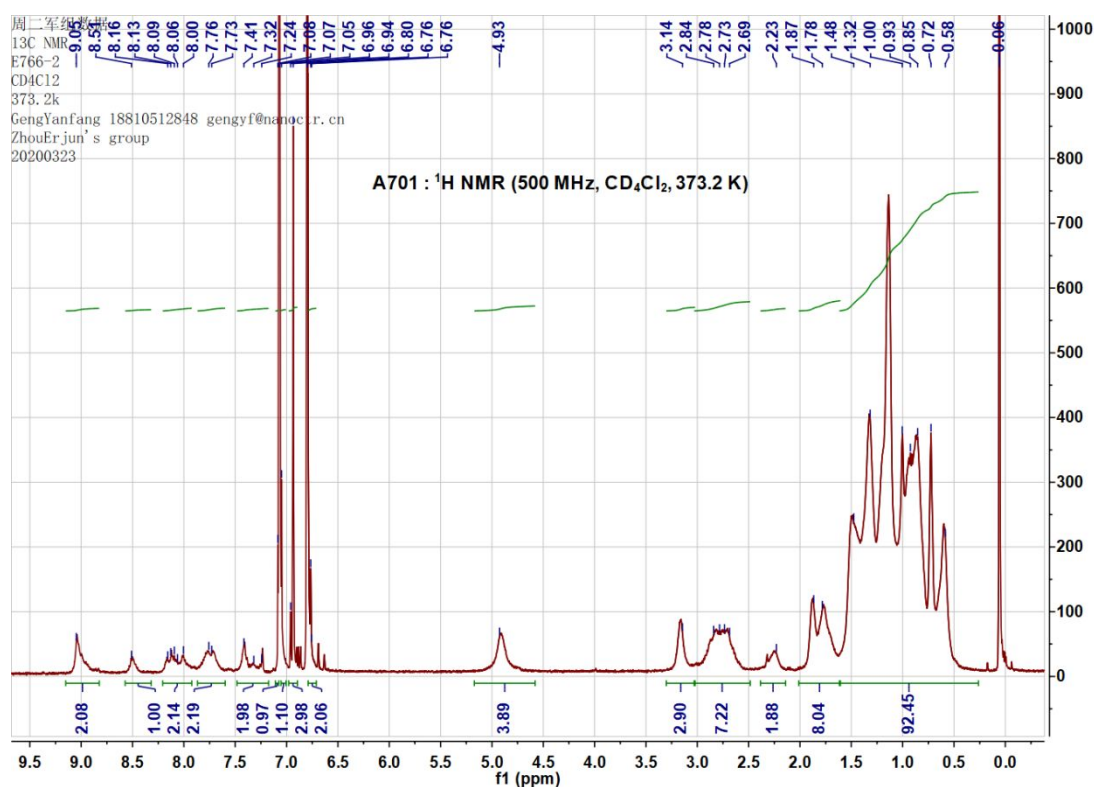


**Figure S3.**  $^1\text{H}$  NMR of **monomer 3** and the enlarged detail view.

### Synthesis polymer of A701

In a 50 mL dry flask, compound 2 (82.5 mg, 0.050 mmol), compound 3 (53.6 mg,

0.050 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (2.89 mg) were dissolved in degassed toluene (10 mL) under nitrogen. The mixture was bubbled with nitrogen for 10 min and then slowly heated to 108 °C. After stirring for 15 h at this temperature, the reaction mixture was cooled down and precipitated into methanol. The polymer was collected by filtration, and washed in a Soxhlet extractor with methanol, hexane and dichloromethane. The dichloromethane fraction was precipitated in methanol, dried under vacuum at 50 °C overnight (50.1 mg, 44.8% yield). Mw = 18.6 kDa, PDI = 2.08.



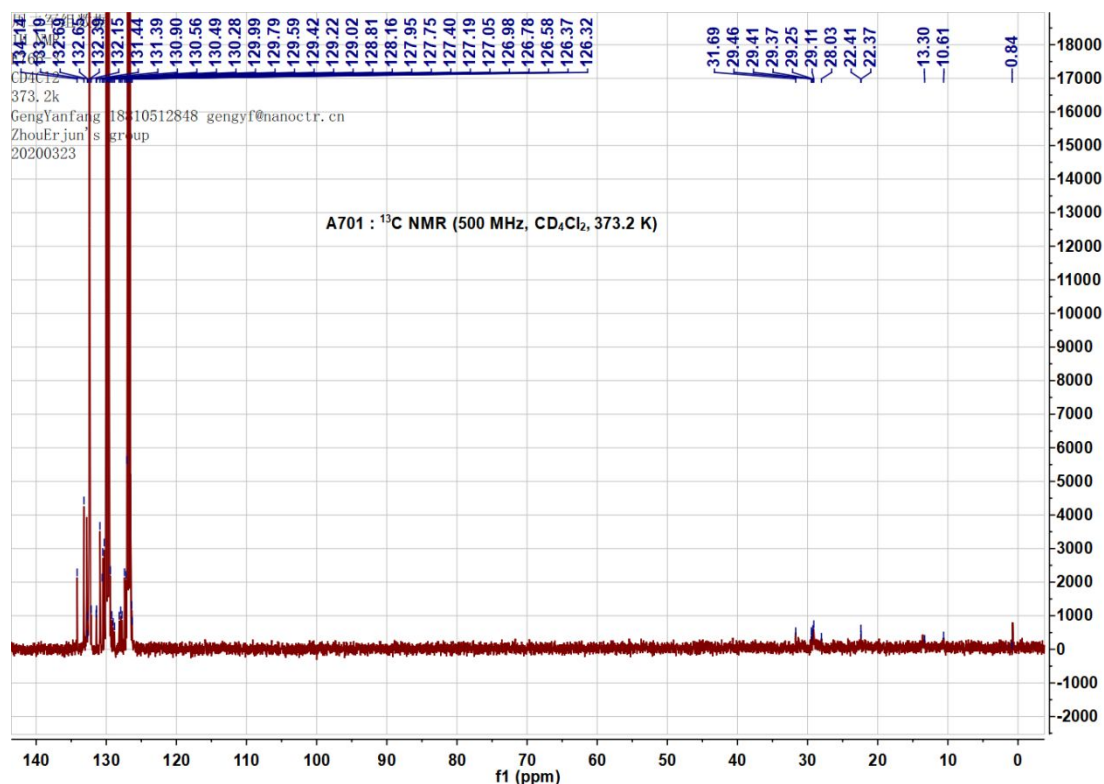


Figure S4. <sup>1</sup>H NMR (373.2K) and <sup>13</sup>C NMR (373.2K) spectra of A701, the solvent is 1,2-dichlorobenzene-d<sub>4</sub> (CD<sub>4</sub>Cl<sub>2</sub>).

### Size exclusion chromatography (SEC) measurements

Size exclusion chromatography (SEC) was performed on an Agilent PL-GPC 220 Integrated High Temperature GPC/SEC System with refractive index and viscometer detectors. The columns are 3 PLgel 10  $\mu$ m MIXED-B LS 300  $\times$  7.5 mm columns. The eluent was 1,2,4-trichlorobenzene. The working temperature was 150 °C. The molecular weights were calculated according to relative calibration with polystyrene standards.



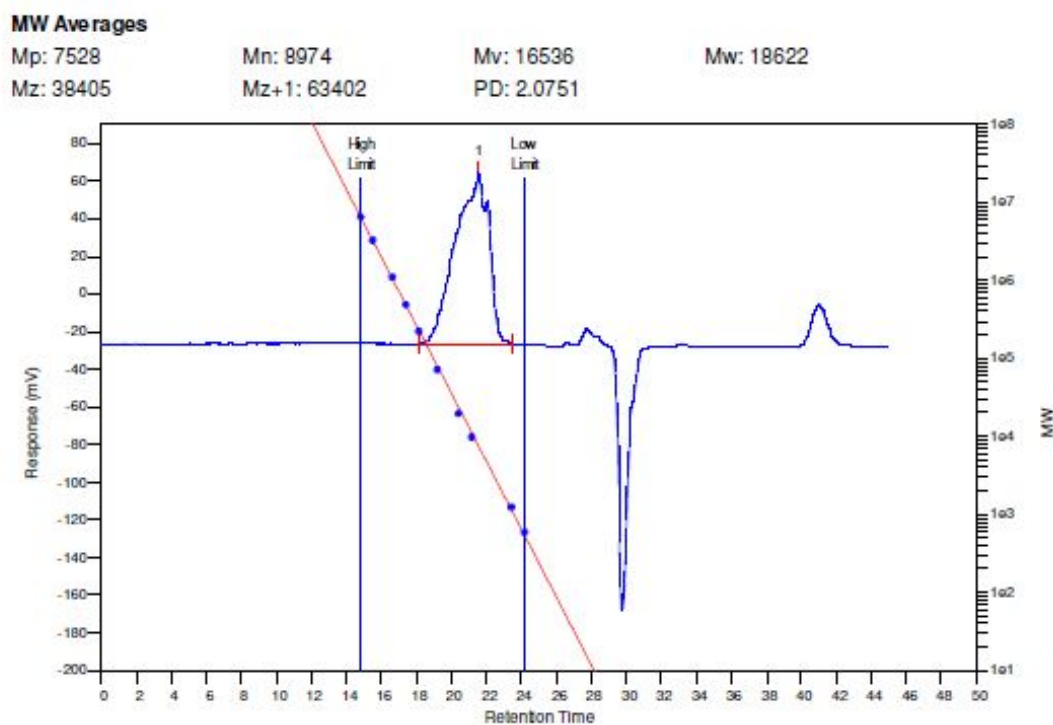
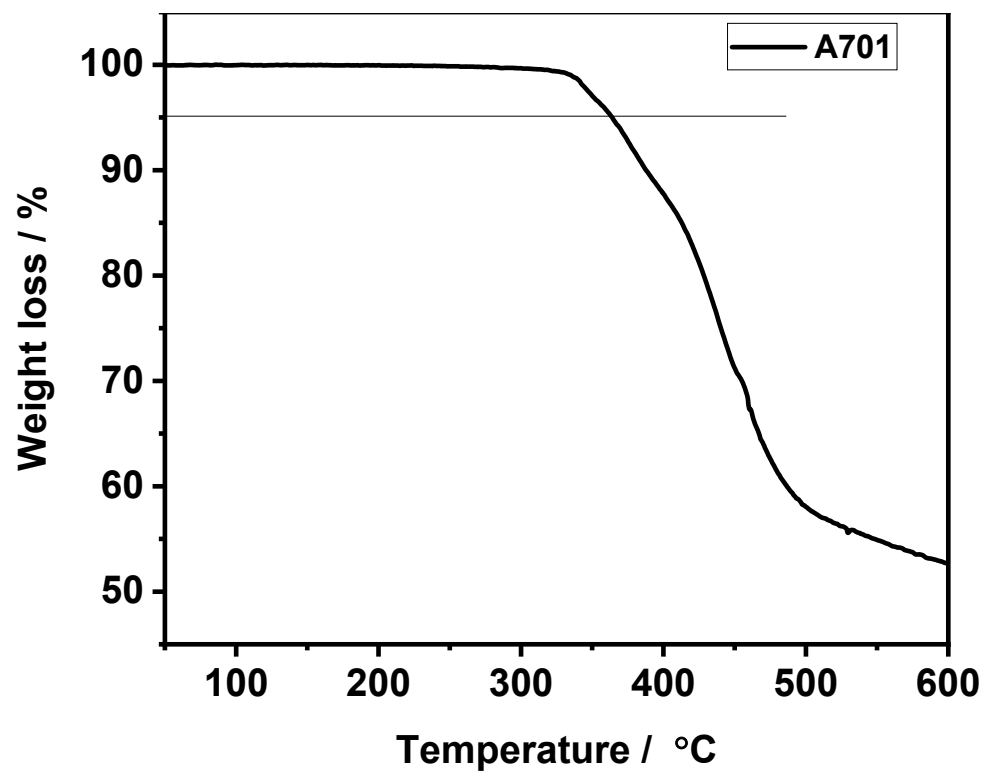


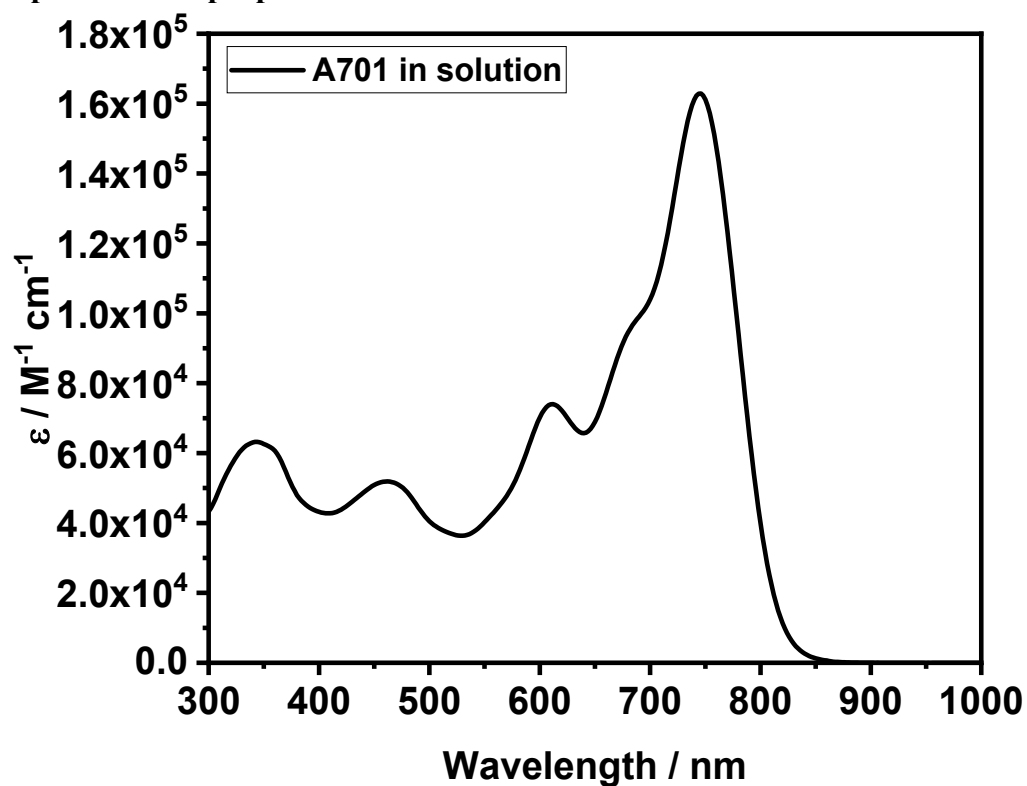
Figure S5. The gel permeation chromatography (GPC) chromatogram for the polymer from the DCM.

### Thermal properties



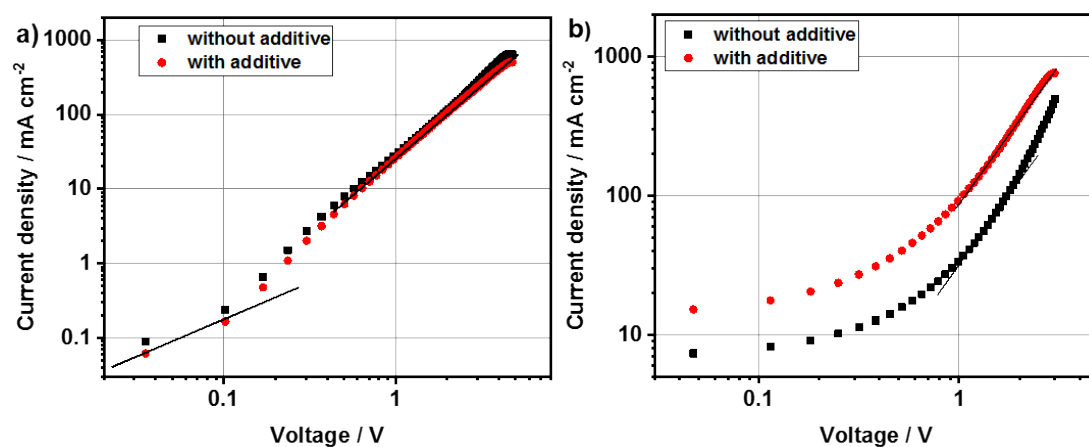
**Figure S6.** TGA curves of **A701** with a scanning rate of 10 °C min<sup>-1</sup> under an atmosphere of N<sub>2</sub>.

### Optoelectrical properties



**Figure S7.** The UV-vis absorption spectra of **A701** in chloroform solution.

### Carriers mobilities



**Figure S8.** (a) Hole and (b) electron mobility plots from SCLC methods. Note: the black represents the films without additive; the red represents the active layer with 3% DIO as solvent additive.

### Photovoltaic performance

**Table S1.** The photovoltaic performance of PBDB-T:A701 under different D/A ratios after thermal annealing at 110 °C, 10 min.

Solvent	D/A	$V_{OC}$ (V)	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
CF 15mg/mL	1.5:1	0.88	13.45	42.64	5.07
	1:1	0.88	15.25	45.90	6.17
	1:1.5	0.89	15.73	50.00	7.06
	1:2	0.89	15.89	46.83	6.65

**Table S2.** The photovoltaic performance of PBDB-T:A701 under different solvent with 1:1.5 (D:A), 3%DIO, after thermal annealing at 110 °C, 10 min.

devices	solvent	$V_{OC}$ (V) <sup>a</sup>	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
PBDB-T:A701	CF	0.92	17.81	61.74	10.08
	CB	0.93	12.11	57.17	6.47
	xylene	0.91	10.49	53.15	4.97

**Table S3.** The photovoltaic performance of PBDB-T:A701 under different solvent additive with 1:1.5 (D:A) and thermal annealing at 110 °C

Solvent	Additive	$V_{OC}$ (V) <sup>a</sup>	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
CF 15mg/mL	1%CN	0.89	14.29	48.48	6.15
	1%DPE	0.88	16.10	45.21	6.43
	1%DIO	0.90	17.64	54.73	8.69
	2%DIO	0.90	18.62	57.61	9.68
	3%DIO	0.92	18.23	61.26	10.26
	4%DIO	0.91	17.23	60.49	9.45
	5%DIO	0.91	18.59	57.81	9.76

**Table S4.** The photovoltaic performance of PBDB-T:A701 under different thermal annealing temperature with 1:1.5 (D:A) and 3%DIO as solvent additive.

devices	Thermal annealing	$V_{OC}$ (V) <sup>a</sup>	$J_{SC}$ (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
CF 15mg/mL 3%DIO	110°C	0.92	18.23	61.26	10.26
	130°C	0.92	18.27	64.01	10.70