Supporting Information

The Role of Chemical Structure in Indacenodithienothiophene-*alt*-Benzothiadiazole Copolymers for High Performance Organic Solar Cells With Improved Photo-Stability Through Minimization of Burn-in Loss

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Experimental Section

Materials

All reactions are air and light sensitive and, therefore, were performed under argon and in the dark. All glassware was washed using detergent (Teepol), rinsed with excess water, acetone and methylene dichloride and dried in an oven at 120 °C. All solvents and reagents were purchased from Aldrich. Toluene was distilled using calcium hydride (CaH₂) and benzophenone prior to polymerization.

The syntheses of bis(trimethylstannyl)tetrahexylphenyl-IDTT (M1), 4,7dibromobenzo[c][1,2,5]thiadiazole (M3), 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (M4) and 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (M5) were performed according to already published procedures.^{S1-S4} Bis(trimethylstannyl)tetrahexylthienyl-IDTT (M2) was purchased from Solarmer Materials Inc.

The general experimental condition for the polymerizations is analytically described below:

The bis(trimethylstannyl)tetrahexylphenyl-IDTT (M1) or bis(trimethylstannyl)tetrahexylthienyl-IDTT (M2) (0.5 mmol) were combined with either 4,7dibromobenzo[c][1,2,5]thiadiazole (M3) or 4,7-dibromo-5-fluorobenzo[c][1,2,5]thiadiazole (M4) or 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (M5) (0.5 mmol) and dissolved in dry toluene (0.025 M). Then, tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba₃)] (0.02 equiv) and tri(o-tolyl)phosphine [P(o-tol)₃] (0.08 equiv) were added and the reaction mixture was stirred at 110°C under argon atmosphere for 48 h. The polymers were purified by precipitation in methanol, filtered and washed using a Soxhlet apparatus with methanol, acetone, hexane, chloroform and chlorobenzene. The chloroform (CTL4) and chlorobenzene (CTL1, CTL2, CTL3, CTL5 and CTL6) fractions were evaporated under reduced pressure and the polymers were precipitated in methanol, filtered through 0.45 mm PTFE filter and finally dried under high vacuum, rendering a dark brown solid with metallic appearance. The yields of the resulting polymers are the following: poly[(tetrahexylphenyl)IDTT-*alt*-BTD] (CTL1) = 65%, poly[(tetrahexylphenyl)IDTT-*alt*-5-fluoroBTD] (CTL2) = 78%, poly[(tetrahexylphenyl)IDTT-*alt*-5,6-difluoroBTD] (CTL3) = 86%, poly[(tetrahexylthienyl)IDTT-*alt*-BTD] (CTL4) = 83%, poly[(tetrahexylthienyl)IDTT-*alt*-5fluoroBTD] (CTL5) = 77% and poly[(tetrahexylthienyl)IDTT-*alt*-5,6-difluoroBTD] (CTL6) = 86%.

Instrumentation

Gel Permeation Chromatography (GPC): Average molecular weights per number (\overline{M}_n) and dispersity (\overline{D}) were determined with GPC at 150 °C on a high temperature PL-GPC 220 system using a PL-GEL 10 μ m guard column, two PL-GEL 10 μ m Mixed-B columns and orthodichlorobenzene (*o*-DCB) as the eluent. The instrument was calibrated with narrow polystyrene standards with M_p ranging from 4830 g/mol to 3242000 g/mol.

Cyclic Voltammetry: Cyclic voltammetry analyses were carried out with a BioLogic VSP potentiostat using platinum electrodes at a scan rate of 100 mV/s in an inert (nitrogen) atmosphere. The measurements were performed on polymer thin films drop-casted from o-DCB solutions onto a platinum working electrode. A Pt wire was used as counter electrode and Ag/Ag⁺ as reference electrode in a 0.1 mol.L⁻¹ solution of recrystallized tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile. Ferrocene was used as internal standard to convert the values obtained with Ag/Ag⁺ reference to the saturated calomel electrode scale (SCE). Both the oxidation (E^{ox}) and reduction (E^{red}) potentials are calculated by $[(E_{p,e}+E_{p,a})/2]$ where $E_{p,e}$ and $E_{p,a}$ are the cathodic and anodic peak potentials, respectively. The E_{HOMO} and E_{LUMO} levels were estimated by $E_{LUMO/HOMO} = -(5.1 + E_{on}^{red/ox})$ eV.^{S5}

Fabrication of photovoltaic devices in standard architecture: All solutions were prepared minimum 24 hours before use and were heated under agitation at 60°C. The ratio by weight polymer:PC₇₁BM is 1:3. The solution concentration (polymer+PC₇₁BM) is 20mg/mL in 1,2-

ortho dichlorobenzene (*o*-DCB). ITO coated glass substrates (Lumtec, 9-15 Ω /sq. 20x20mm²) have been cleaned in four successive ultrasonic baths: firstly into water and soap, secondly by into water, thirdly into acetone and lastly into isopropanol. In order to remove the last organics impurities, substrates has been exposed 30 minutes to UV ozone just before PEDOT:PSS deposition. Spin coating of the PEDOT:PSS (Clevios PVP AI 4083) has been performed with the following parameters: s=5000rpm; a=1000rpm/s; t=60s. The resulting PEDOT:PSS layer has been annealed at 140°C during 30 minutes in a glove box (under nitrogen). On the PEDOT:PSS layer, the active layer was spin coated from hot solution in glove box with the following parameters: s=1000rpm; a=200rpm/s; t=180s. Few minutes before spin coating, 3% (by volume) of chloronaphtalene (CN) as additive were added. The thickness of the different active layer was between 53 nm to 82 nm. Then, the active layer was annealed for 10 min at 110°C prior top electrodes deposition. Finally 20 nm of calcium and 120 nm of aluminium as top electrodes were evaporated by joule effect through appropriate shadow mask at 1x10⁻⁶ mbars. The device active area was 12 mm².

Fabrication of Photovoltaic devices in inverted architecture: All the fabrication steps (cleaning, active layer deposition) have been unchanged. The following structure has been used: ITO/zinc oxide (ZnO)/CTL3:PC₇₁BM/ molybdenum oxide (MoO₃)/Ag. Zinc oxide nanoparticles (Nanograde Ltd.) were spin coated on top of the ITO glass from 2-propanol dispersion (2.5 wt%, 6000 rpm, 30 s) and annealed (100 °C, 10 min). In the end, 7 nm of molybdenum oxide and 120nm of silver as top electrodes were evaporated.

J-V measurements: Current density versus voltage (J–V) characteristics were measured under darkness and under Air Mass 1.5 Global (AM 1.5 G) with an irradiation intensity of 100 mW/cm² by using a solar simulator (ABET - Sun 3000) and a Keithley 2400 Source Measure Unit. J–V characteristics were measured under nitrogen (gloves box) just after devices fabrication.

Stability measurements: The solar cells were placed in a sealed, electronically controlled degradation chamber with regulated environment ($O_2 < 1$ ppm, $H_2O < 1$ ppm). The J-V characteristics of the devices were probed periodically while continuously light-soaked using white light LEDs irradiating at 100 mW/cm².



Light spectrum of the LEDs used in this work (3000K, 80 CRI) as extracted from the company's datasheet.

Absorption spectrometry: In-situ UV-Vis temperature dependent experiments in solution were performed using Agilent Cary Spectrophotometer. Polymers were dissolved in *o*-DCB solutions at relatively low concentrations (0.01-0.015 mg/mL for both) to ensure transparency. Polymer thin-film (drop-casted from *o*-DCB solutions onto glass plates) absorptions as well as the absorption spectra of polymer:PC₇₁BM thin films as deposited onto ITO/PEDOT:PSS before (0h) and after 48h of photo-degradation were recorded on a Shimadzu UV-2600 absorption spectrometer.

microRAMAN: The micro-RAMAN spectra of polymer: $PC_{71}BM$ thin films as deposited onto ITO/PEDOT:PSS before (0h) and after 48h of photo-degradation were recorded on an inVia RAMAN microscope of Renishaw industries. The RAMAN microscope was equipted with a solid state laser of 785nm, 50x lens and optical table. Multiple scans for each sample where performed during acquisition of the spectra.

Space Charge Limited Current (SCLC) measurements: Hole-only and electron-only SCLC devices were elaborated to investigate the out-of-plane mobility. The device elaboration and characterization were performed at room temperature in a nitrogen-filled glove box. The hole and electron mobility are extracted using the standard expression for charge space limited current density following the Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

Where ε_0 is the permittivity of free space, ε_r is the polymer dielectric constant, μ_h is the hole mobility, V is the voltage drop across the device and L is the film thickness.

SCLC: The device following: Hole-only structure the was ITO/PEDOT:PSS/polymer/MO₃/Ag. The ITO layer was cleaned sequentially by ultrasonic treatments in acetone, isopropyl alcohol and deionized water. After an additional 30 minutes exposure to ultra-violet generated ozone, a 30 nm thick PEDOT:PSS layer was spin-coated from an aqueous solution on top of the ITO layer and dried for 30 min at 140°C. o-DCB polymer solutions of varying concentration were prepared and stirred at room temperature for 24h. The active layer was spin coated from hot solution on top of the PEDOT-PSS layer. The devices were completed by thermal evaporation of 7 nm molybdenum oxide and 120 nm silver as top electrode.

<u>Electron-only SCLC:</u> The device structure was the following: ITO/PEIE/polymer/Ca/Al. The ITO layer was cleaned sequentially by ultrasonic treatments in acetone, isopropyl alcohol and deionized water. After an additional 30 minutes exposure to ultra-violet generated ozone, a solution of PEIE diluted in 2-methoxyethanol (0.6% wt) is deposited on top the ITO (5000 rpm, 60s) dried for 10 min at 100°C. Orthodichlorobenzene polymer solutions of varying concentration were prepared and stirred at room temperature for 24h. The active layer was spin coated from hot solution on top of the PEIE layer. The devices were completed by thermal evaporation of 20 nm of calcium and 120 nm of aluminium as top electrode.

Transient absorption spectroscopy (TAS) measurements were performed on a Newport (TAS-1) transient absorption spectrometer, equipped with a source pulsed laser beam generated from an Yb:KGW-based laser system (PHAROS, Light Conversion), emitting at 1026 nm, with a pulse duration of 170 fs and 1 KHz repetition rate. The fundamental beam is split, so that the probe beam component (10% of the source) passes through a delay line and routed on a YAG crystal, which generates a supercontinuum white light of 520-900 nm. The other part of the incident beam (90% of the source), is used as the pump beam for sample excitation. The energy of the pump beam can be controlled by a variable reflective neutral density filter inside the TAS instrument, or by altering the power of the employed 1026 nm fundamental laser beam. For all measurements, the probe light is coupled through an optical fiber to a multichannel detector and monitored as a function of wavelength. In a typical TAS pump-probe experiment, the sample is excited by the pump beam, and the corresponding decay dynamics of the sample's relative optical density are recorded as a function of wavelength at various time delays after photo-excitation.

High resolution transmission electron microscopy (HR-TEM): Transmission electron microscope (TEM) images were obtained in bright field mode at 200 kV using a high resolution (HR) JEOL-2100 microscope . In case of TEM samples, glass/ITO/PEDOT:PSS/blend films before (0h) and after 48h of photo-degradation were transferred to distilled water, and the floated blend films transferred to the carbon coated Cu grids (200 mesh, Polysciences Inc.).



Fig. S1 Gel permeation chromatography (GPC) profiles of CTL1-3 (left) and CTL4-6 (right).

Polymer	Average Molecular Weight per Number [${}^{ar{M}_n}$] (g/mol)	Average Molecular Weight per Weight [$ar{M}_w$] (g/mol)	Dispersity [Đ]
CTL1	182500	583850	3.2
CTL2	108300	312500	2.9
CTL3	65300	390300	6.0
CTL4	13150	43400	3.3
CTL5	24400	51800	2.1
CTL6	36700	86700	2.4

 Table S1 Molecular weight characteristics of the CTLs polymers.



Fig. S2 Absorption spectra of CTL1-6 in (a) o-DCB solution, and (b) as thin films.



Fig. S3 Cyclic voltammetry graphs of (a) CTL1-3 and (b) CTL4-6 as thin films.





Fig. S4 Dark J-V curves of (a) hole-only and (b) electron-only devices for polymer: $PC_{71}BM$ 1:3 systems. The dotted thick line is the expected dependence of J as a function of V² for the SCLC regime.



Fig. S5 Absorption spectra of pristine (0 h) and photo-oxidative blend (polymer:PC₇₁BM) films under 1 sunlight illumination for 48 h of (a) CTL1, (b) CTL2, (c) CTL3, (d) CTL4, (e) CTL5 and (f) CTL6.







Fig. S6 Micro-RAMAN spectra of pristine (0 h) and photo-oxidative blend (polymer: $PC_{71}BM$) films under 1 sunlight illumination for 48 h of (a) CTL1, (b) CTL2, (c) CTL3, (d) CTL4, (e) CTL5 and (f) CTL6.

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