

Supporting Information

All-Polymer Solar Cells with 3.3% Efficiency Based on Naphthalene Diimide-Selenophene Copolymer Acceptor

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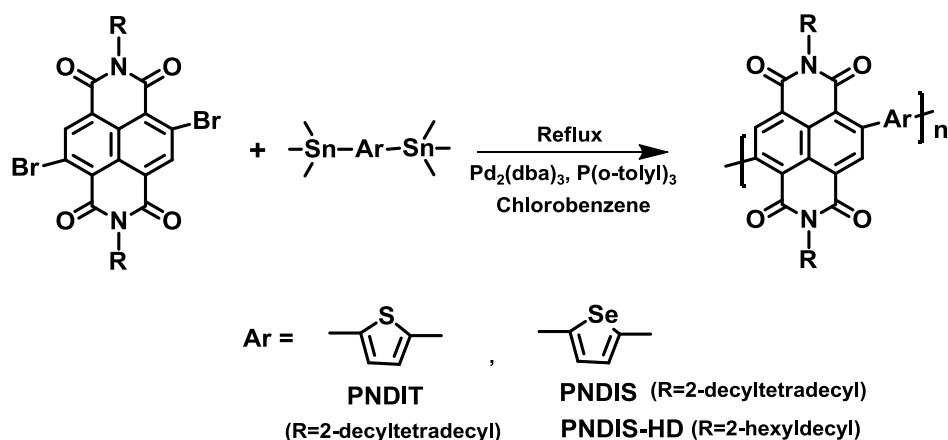


Figure S1. Synthetic route of NDI-copolymers: PNDIT, PNDIS, and PNDIS-HD.

Experimental Methods

2,5-Dibromoselenophene. Selenophene (5 g, 0.038 mol) was added into a 250 mL round-bottom flask. The flask was purged with argon before adding 100 mL of chloroform as a solvent. Afterward, NDS (13.575 g, 0.076 mol) was added in three portions. After stirring the mixture overnight at room temperature in the dark, the reaction was quenched by adding water. The crude product was extracted with chloroform, and purified by column chromatography with hexane. Slightly yellow oil was obtained and used in next step without further purification. 2,5-Dibromoselenophene (7.5 g, 68.3 %), ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 7.02 (2H).

2,5-Bis(trimethylstannyl)selenophene. 2,5-Dibromoselenophene (2 g, 6.92 mmol) was added into a 250 mL round-bottom flask. Afterwards, 50 mL of THF was added under argon atmosphere. The mixture was cooled to -78°C in a dry ice bath and 2.5 M butyllithium solution in hexane (6.1 mL, 15.23 mmol) was added dropwise. After stirring the mixture for an hour at -

78 °C, 1 M trimethyltinchloride solution in THF (15.9 mL, 15.9 mmol) was added in one portion at -78 °C. Dry ice bath was removed after 5 min and the mixture was warmed up to room temperature. After stirring overnight at room temperature, the reaction mixture was poured into water and extracted with diethyl ether two times. The organic phase was dried with sodium sulfate anhydrous and the solvent was evaporated by using a vacuum rotary evaporator. After reprecipitation in MeOH, a white solid was obtained and subsequently used in polymerization without further purification (500 mg; yield = 15.8 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.72 (2H), 0.3 - 0.48 (18H). Melting point (*T*_m): 122 °C.

2,5-Bis(trimethylstannyl)thiophene. 2,5-Dibromothiophene (1.5 g, 6.2 mmol) was added into a 250 mL round-bottom flask. Afterwards, 40 mL of THF was added under argon atmosphere. The mixture was cooled to -78 °C in a dry ice bath and 2.5 M butyllithium solution in hexane (5.95 mL, 14.88 mmol) was added dropwise. After stirring the mixture for an hour at -78 °C, 1 M trimethyltinchloride solution in THF (15.5 mL, 15.5 mmol) was added in one portion at -78 °C. Dry ice bath was removed after 5 min and the mixture was warmed up to room temperature. After stirring overnight at room temperature, the reaction mixture was poured into water and extracted with diethyl ether two times. The organic phase was dried with sodium sulfate anhydrous and the solvent was evaporated by using a vacuum rotary evaporator. After reprecipitation in MeOH, a white solid was obtained and subsequently used in polymerization without further purification (1 g; yield = 39.2 %). ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.46 (2H), 0.34 - 0.52 (18H). Melting point (*T*_m): 95 °C

Poly{[N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-selenophene} (**PNDIS**). 4,9-Dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (480.6 mg, 0.44 mmol), 2,5-bis(trimethylstannyl)selenophene (200 mg, 0.44 mmol), Pd₂(dba)₃ (8 mg, 0.0088 mmol) and P(*o*-tolyl)₃ (10.7 mg, 0.035 mmol) were added into a 100 mL three-neck round-bottom flask. The flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, 22 mL of chlorobenzene was added and degassed and filled with argon three times. The reaction mixture was refluxed for 72 h under argon. After cooling down to room temperature, the polymerization mixture was poured and stirred into 200 mL methanol and 5 mL hydrochloric acid solution for 3 h. The polymer precipitated out as a dark reddish purple solid and was filtered using a filter paper. The polymer was purified by Soxhlet extraction with methanol, hexane, and acetone. **PNDIS** (365 mg; yield = 81.9 %), ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 9.1 (2H), 7.7 (2H), 4.2 (4H), 2.1 (2H), 0.9–1.5 (92H). GPC: *M*_w = 31.5 kDa, *M*_n = 26.1 kDa, PDI = 1.2. TGA: *T*_d = 415 °C.

Poly{[N,N'-bis(2-hexyldecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-selenophene} (**PNDIS-HD**). 4,9-Dibromo-2,7-bis(2-hexyldecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (200 mg, 0.23 mmol), 2,5-bis(trimethylstannyl)selenophene (104.6 mg, 0.23 mmol), Pd₂(dba)₃ (4.2 mg, 0.0046 mmol) and P(*o*-tolyl)₃ (5.6 mg, 0.0184 mmol) were added into a 100 mL three-neck round-bottom flask. The

flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, 10 mL of chlorobenzene was added and degassed and filled with argon three times. The reaction mixture was refluxed for 72 h under argon. After cooling down to room temperature, the polymerization mixture was poured and stirred into 200 mL methanol and 5 mL hydrochloric acid solution for 3 h. The polymer precipitated out as a dark reddish purple solid and was filtered using a filter paper. The polymer was purified by Soxhlet extraction with methanol, hexane, and acetone. **PNDIS-HD** (165 mg; yield = 82.3 %), ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 9.15 (2H), 7.8 (2H), 4.2 (4H), 2.05 (2H), 0.8-1.5 (60H). GPC: M_w = 177.9 kDa, M_n = 79 kDa, PDI = 2.3. TGA: T_d = 400 °C.

Poly{[N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-thiophene} (**PNDIT**). 4,9-Dibromo-2,7-bis(2-decyltetradecyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8-tetraone (350 mg, 0.32 mmol), 2,5-bis(trimethylstannyl)thiophene (130.7 mg, 0.32 mmol), $\text{Pd}_2(\text{dba})_3$ (5.84 mg, 0.0064 mmol) and $\text{P}(o\text{-tolyl})_3$ (7.77 mg, 0.026 mmol) were added into a 100 mL three-neck round-bottom flask. The flask equipped with a condenser was then degassed and filled with argon three times. Afterwards, 15 mL of chlorobenzene was added and degassed and filled with argon three times. The reaction mixture was refluxed for 72 h under argon. After cooling down to room temperature, the polymerization mixture was poured and stirred into 200 mL methanol and 5 mL hydrochloric acid solution for 3 h. The polymer precipitated out as a dark reddish purple solid and was filtered using a filter paper. The polymer was purified by Soxhlet extraction with methanol, hexane, and acetone. **PNDIT** (310 mg; yield = 92.3 %), ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 9.0 (2H), 7.5 (2H), 4.2 (4H), 2.1 (2H), 0.8-1.45 (92H). GPC: M_w = 31.6 kDa, M_n = 23.9 kDa, PDI = 1.3. TGA: T_d = 430 °C.

Characterization. The molecular structure and physical properties of PNDIBS and PNDIBT were investigated by ^1H NMR, gel permeation chromatography (GPC) analysis, thermogravimetric analysis (TGA), and X-ray diffraction (XRD). ^1H NMR spectra at 300 MHz were recorded on a Bruker-AF300 spectrometer. GPC analysis of the copolymers was performed on GPC Model 120 (DRI, PLBV400HT viscometer) against polystyrene standards in chlorobenzene at 60 °C. TGA thermograms were obtained on a TA Instruments Q50 TGA at a heating rate of 20 °C/min under nitrogen gas flow. XRD data were obtained from Bruker D8 Discover with a Cu $K\alpha$ beam using GADD XRD system, and the samples were prepared by drop-casting of polymer solutions in chloroform onto glass substrates followed by annealing at 200 °C for 10 min. Optical and electrochemical properties were investigated by UV-vis absorption spectroscopy and cyclic voltammetry. Absorption spectra were measured on a PerkinElmer model Lambda 900 UV/vis/near-IR spectrophotometer. Solution and solid state absorption spectra were obtained from polymer solutions in chloroform and as thin films on glass substrates, respectively. Cyclic voltammetry (CV) experiments were done on an EG&G Princeton Applied Research potentiostat/galvanostat (model 273A) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile at a scan rate of 100 mV/s. A three-electrode cell was used in this analysis. Platinum wires were used as counter and

working electrodes, and Ag/Ag^+ (Ag in 0.1 M AgNO_3 solution, Bioanalytical System, Inc.) was used as a reference electrode. Ferrocene/ferrocenium was used as an internal standard by running CV at the end, and this data was used to convert the potential to saturated calomel electrode (SCE) scale. The films of the copolymer were coated onto the Pt wires by dipping the wires into 1 wt % polymer solutions in chloroform.

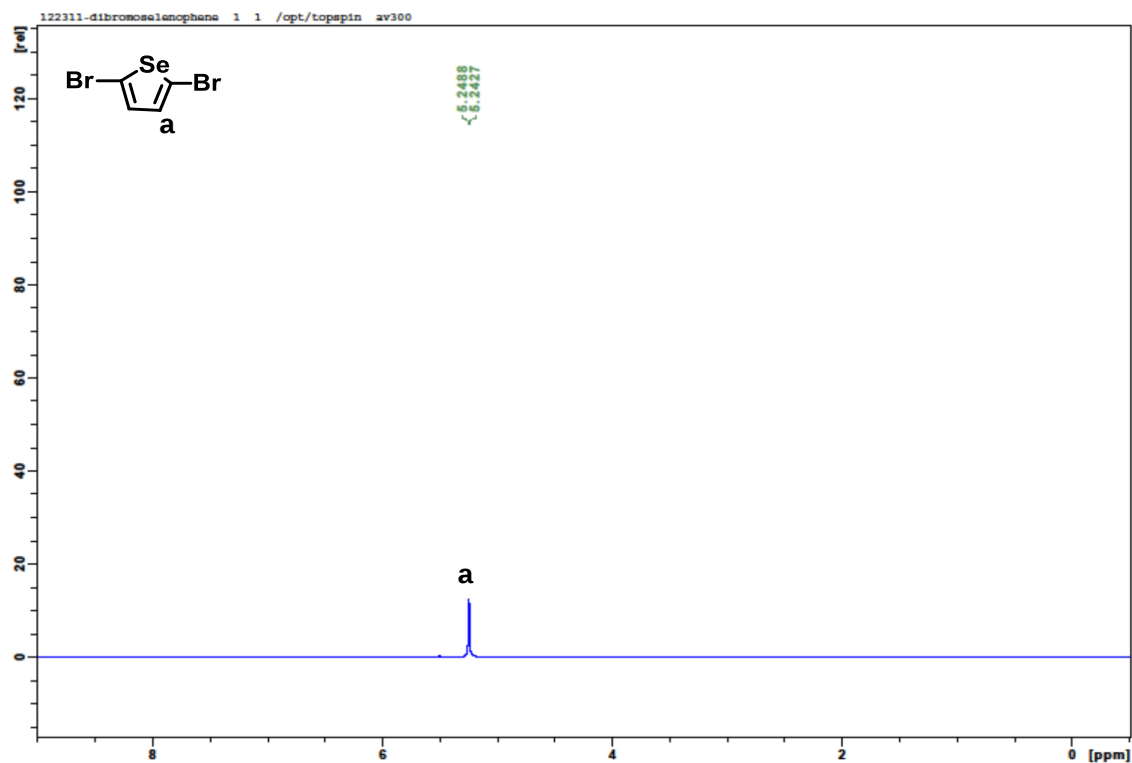


Figure S2. ^1H NMR spectrum of 2,5-dibromoselenophene.

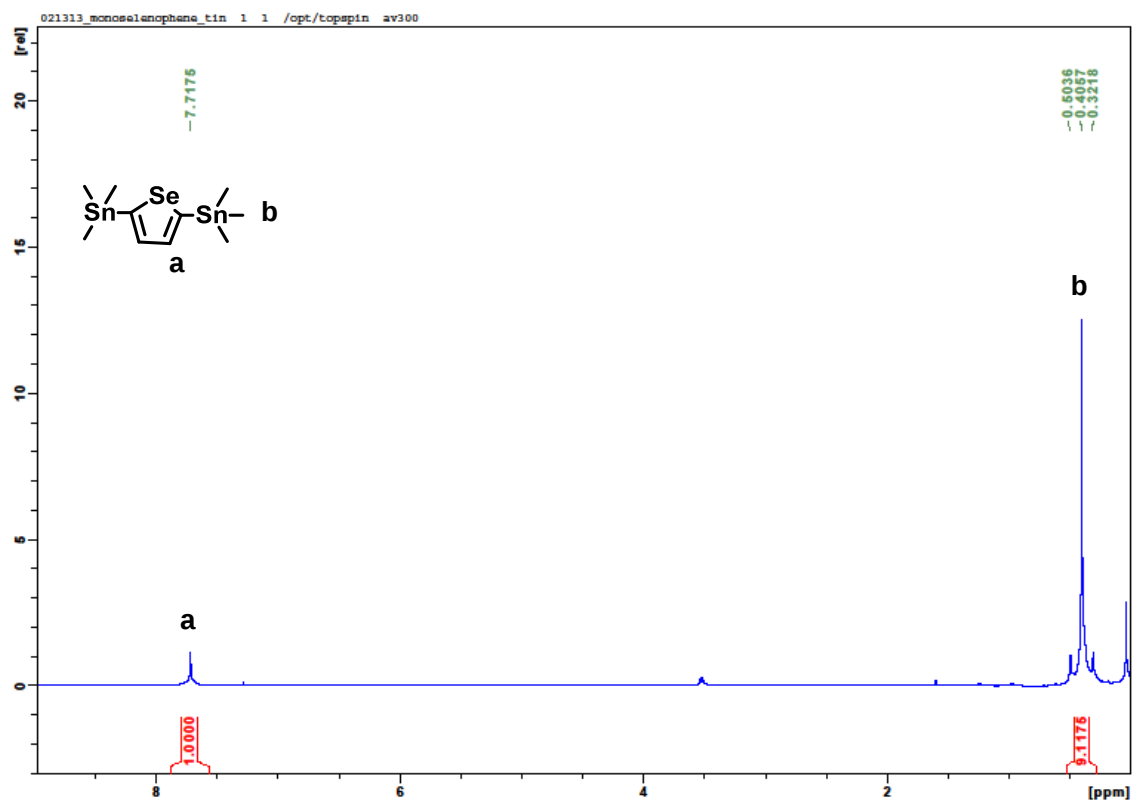


Figure S3. ^1H NMR spectrum of 2,5-bis(trimethylstannyl)selenophene.

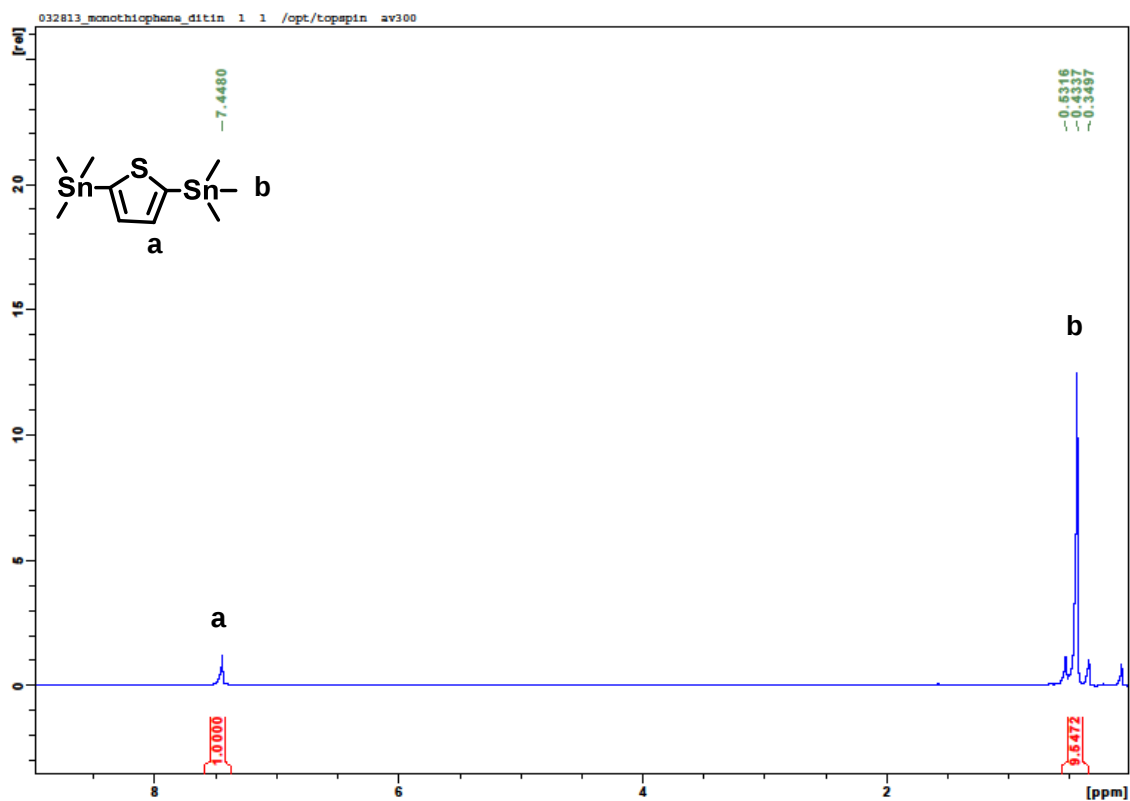


Figure S4. ^1H NMR spectrum of 2,5-bis(trimethylstannyl)thiophene.

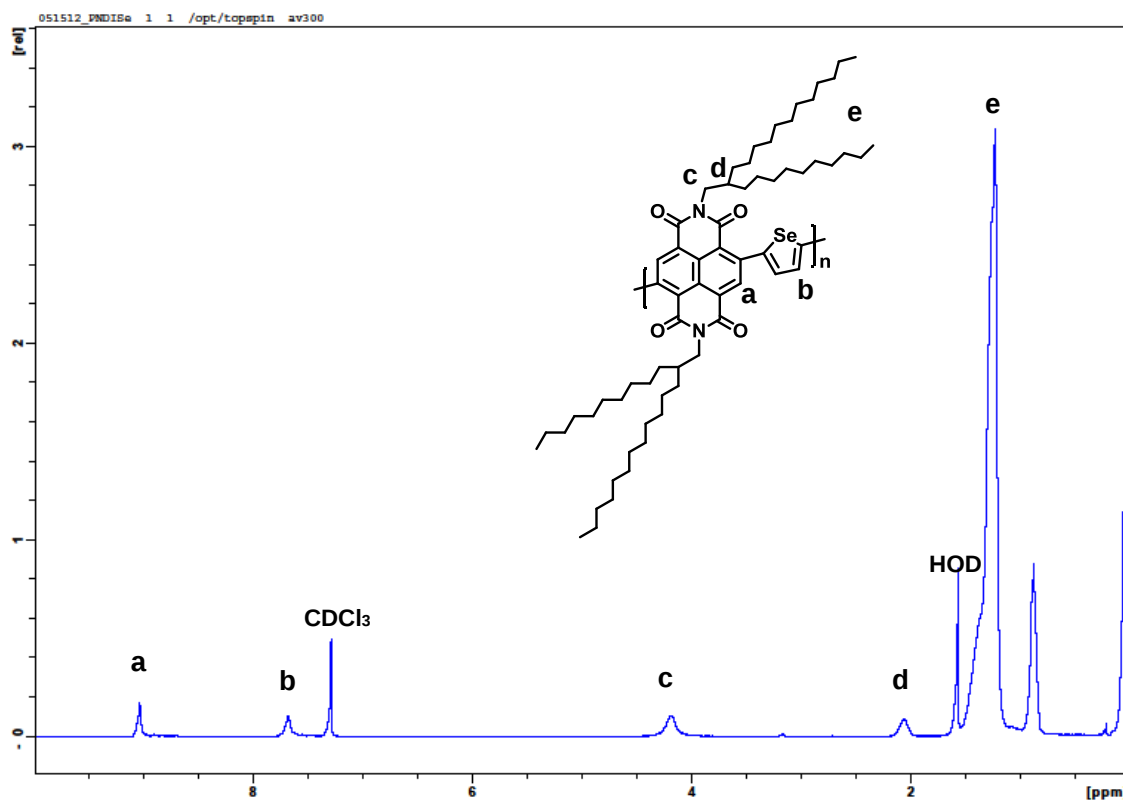


Figure S5. ^1H NMR spectrum of poly{[N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-selenophene} (**PNDIS**).

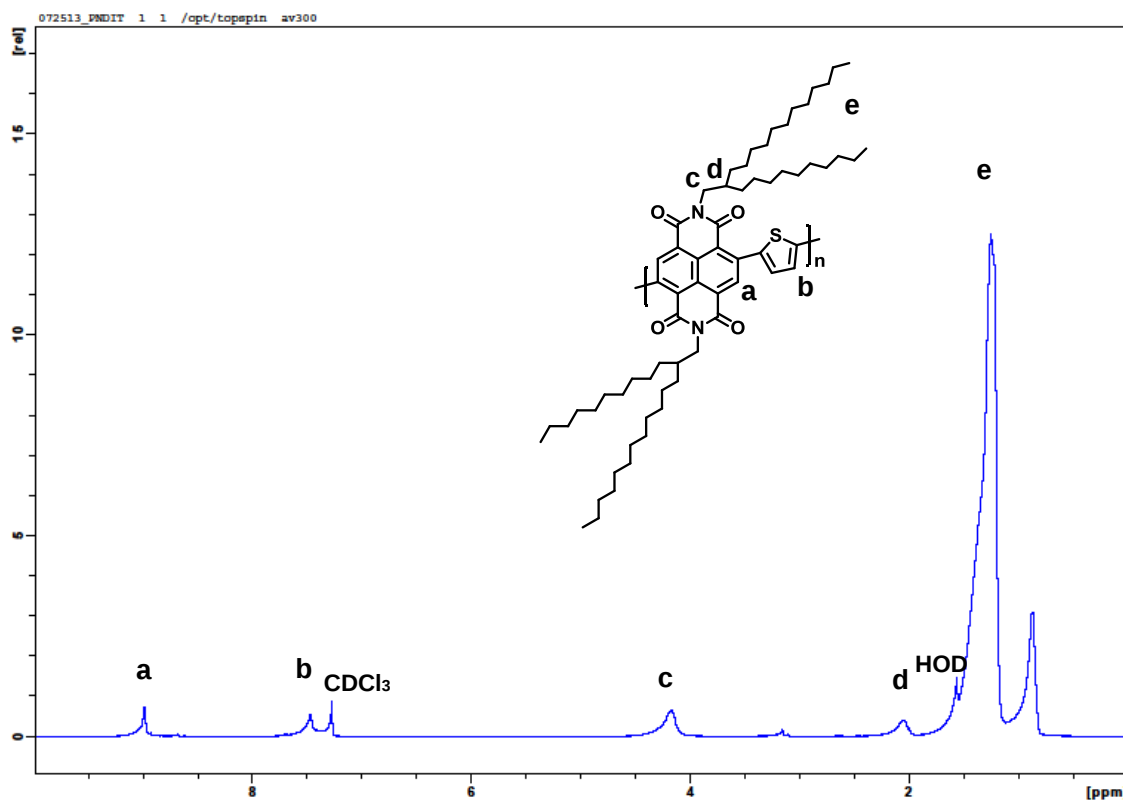


Figure S6. ^1H NMR spectra of poly{[N,N'-bis(2-decyltetradecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-thiophene)} (**PNDIT**).

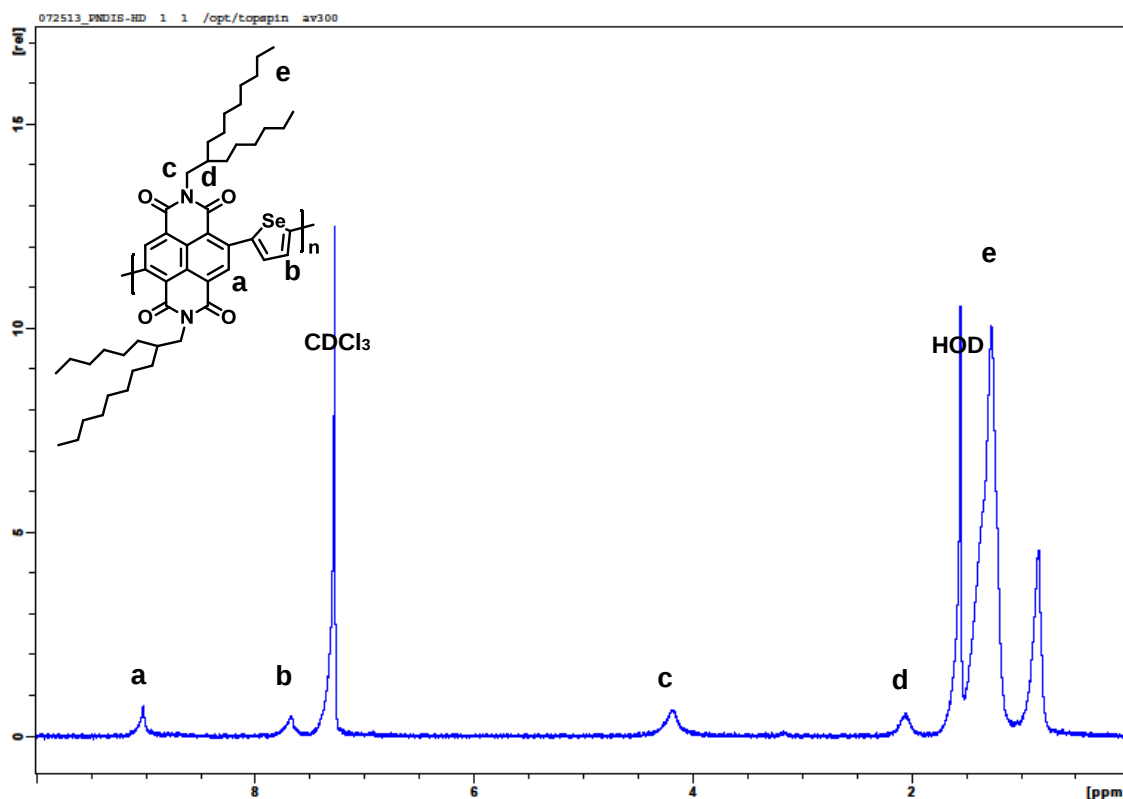


Figure S7. ^1H NMR spectrum of poly{[N,N'-bis(2-hexyldexyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-*alt*-5,5'-selenophene)} (PNDIS-HD).

Fabrication and Characterization of Inverted Solar Cells. Solar cells with the inverted device structure of ITO/ZnO/active layer/ MoO_3/Ag were fabricated. ITO/glass substrates were cleaned sequentially in ultrasonic baths of acetone, deionized water, and 2-propanol, and then dried at 60 $^\circ\text{C}$ in a vacuum overnight. ITO/glass substrates were treated with oxygen plasma before use. Zinc oxide (ZnO) precursor was prepared as reported in the literature^{S1}, spin-coated on top of the ITO and annealed at 250 $^\circ\text{C}$ for 1 hr in air. The ZnO film thickness was approximately 30 nm which is confirmed by using a profilometer. The active layer was then spin-coated from the polymer mixture solution to make a thin film of 70 nm thickness and thermally annealed at 150 $^\circ\text{C}$ for 10 min in a glovebox. The substrates were then loaded in a thermal evaporator (BOC Edwards, 306) to deposit an anode composed of thin layer of 7.5 nm MoO_3 and 100 nm Ag under high vacuum (8×10^{-7} Torr). Five solar cells, each with an active area of 4 mm^2 , were fabricated per ITO substrate. The current density–voltage (J – V) curves of solar cells were measured using a HP4155A semiconductor parameter analyzer under laboratory ambient air conditions. An AM1.5 illumination at 100 mW/cm^2 was provided by a filtered Xe lamp and calibrated by using an NREL-calibrated Si diode. The external quantum efficiency

(EQE) was measured using a QEX10 solar cell quantum efficiency measurement system (PV Measurements, Inc.) and was calibrated with a NREL-certified Si diode before measurement. Film thickness was measured by an Alpha-Step 500 profilometer (KLA-Tencor, San Jose, CA). AFM characterization of surface morphology was done on a Veeco Dimension 3100 Scanning Probe Microscope (SPM) system. The AFM images were directly measured on the same devices used for J - V characterization.

Fabrication and Characterization of Field-Effect Transistors. Organic field effect transistors (OFETs) with top-contact, bottom-gate geometry were fabricated on heavily n doped <100> silicon wafer (0.002-0.004 Ω/cm) which served as gate electrode while its 200 nm of thermally grown SiO_2 served as gate dielectric ($C \approx 17\text{nF}/\text{cm}^2$). The wafer surface was cleaned and modified with sequential ultrasonication in acetone and isopropanol followed by plasma treatment and surface modification by octyltrichlorosilane (OTS-8). For silane modification, the wafer was spin coated in air with 0.1 M solution of OTS-8 in chloroform at 3000 rpm for 10 seconds, rinsed with toluene and dried at 110 $^\circ\text{C}$ for 10 minutes. The PNDIs based semiconductor polymers were fabricated on the modified substrate by spin coating 8 mg/mL of polymer solution at 2000 rpm for 60 seconds inside of the glove box followed by annealing at 2000 $^\circ\text{C}$ for 10 minutes on the hot plate. The gold source/drain electrodes with channel length (L) of 1000 μm and width (W) of 100 μm were deposited by vacuum evaporation through a shadow mask. All the electrical characteristics of the OFET devices were measured using HP 4145B semiconductor parameter analyzer in nitrogen atmosphere.

Space-Charge-Limited Current (SCLC) Measurement. Current-voltage (J - V) characteristics of the SCLC devices were measured by using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo). The electron mobility was extracted by fitting the J - V curves in the near quadratic region according to the modified Mott-Gurney equation,^{S2}

$$J = \frac{9}{8} \varepsilon \varepsilon_0 \mu \frac{V^2}{L^3} \exp\left(0.89\beta \frac{\sqrt{V}}{\sqrt{L}}\right)$$

where J is the current density, ε_0 is the permittivity of free space, ε is the relative permittivity, μ is the zero-field mobility, V is the applied voltage, L is the thickness of active layer, and β is the field-activation factor.

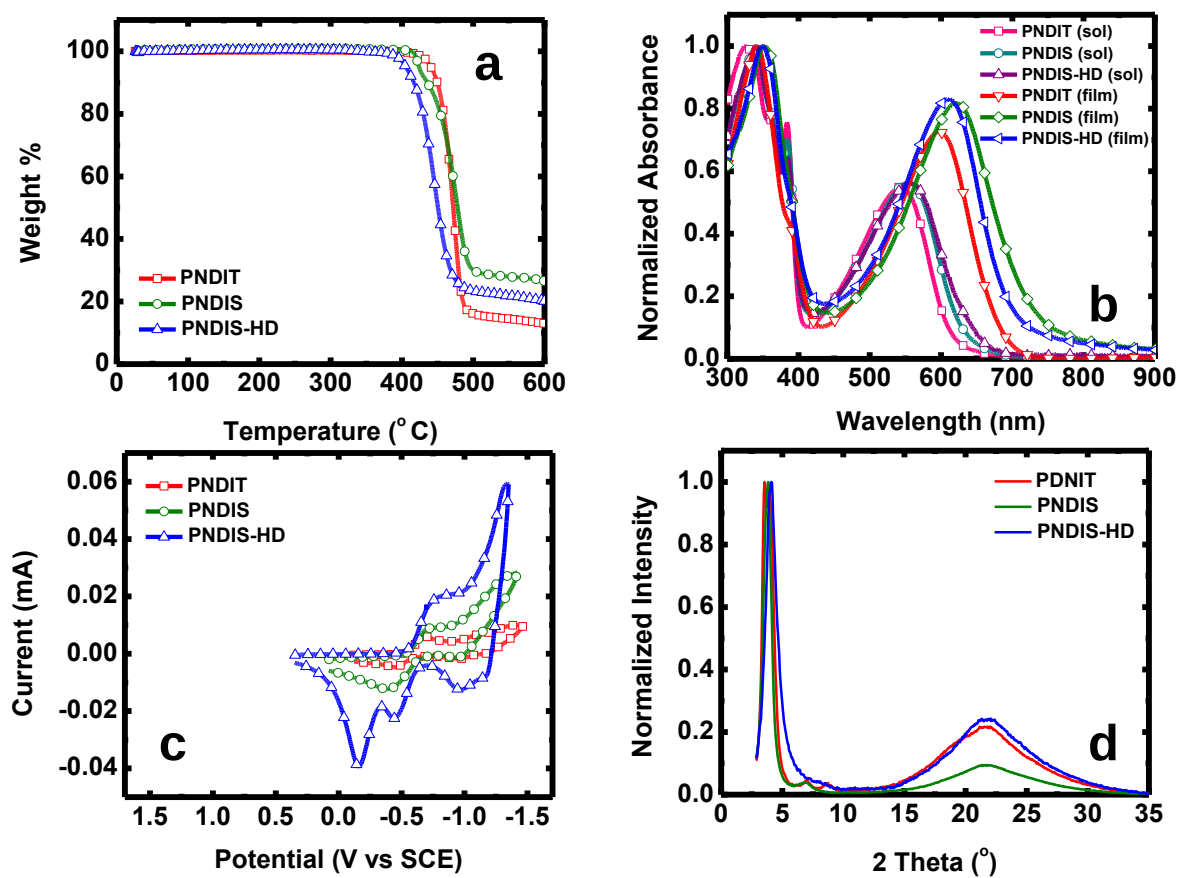


Figure S8. (a) TGA thermograms, (b) UV-vis absorption spectra, (c) cyclic voltammograms, and (d) X-ray diffraction (XRD) patterns of PNDIT, PNDIS, and PNDIS-HD copolymers.

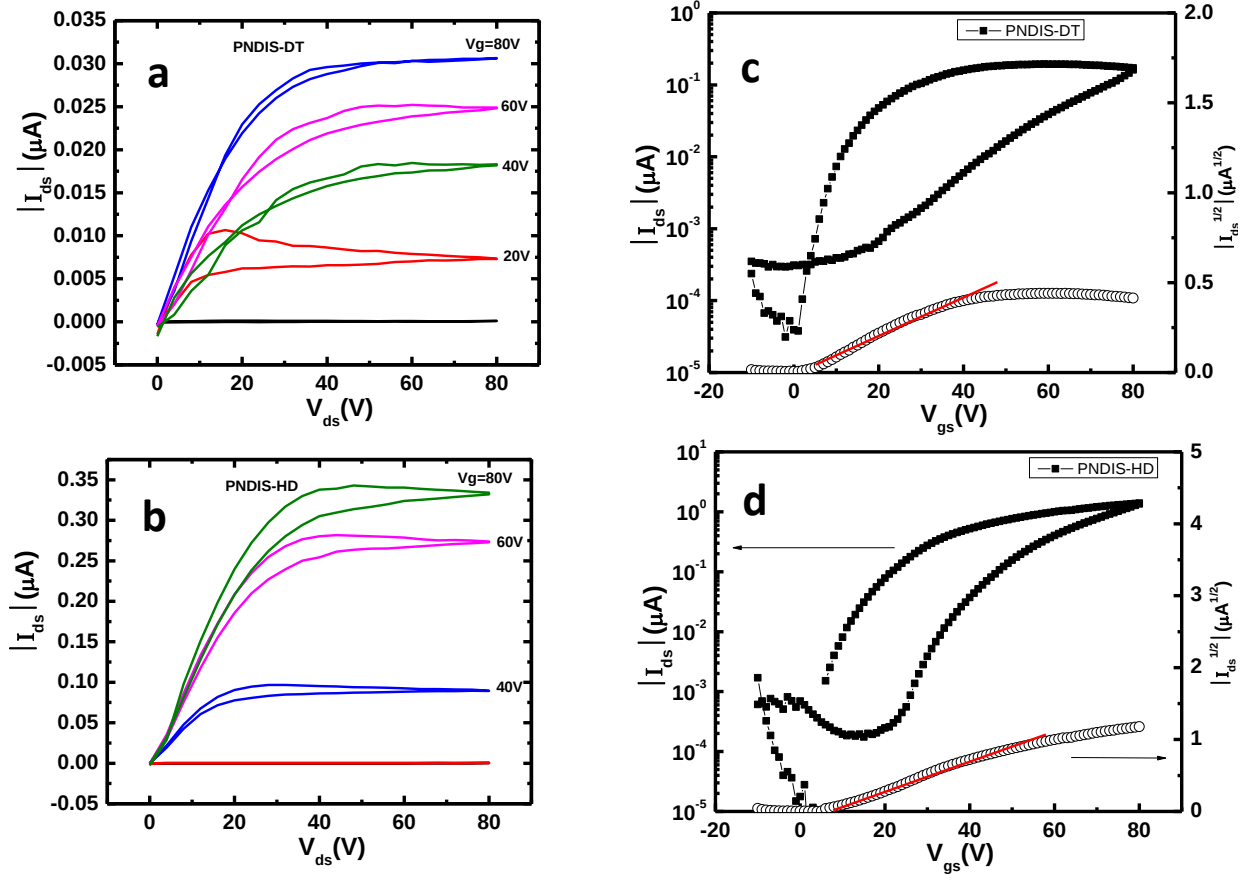


Figure S9. Output characteristics of (a) PNDIS and (b) PNDIS-HD; and transfer characteristics of (c) PNDIS and (d) PNDIS-HD n-channel OFETs.

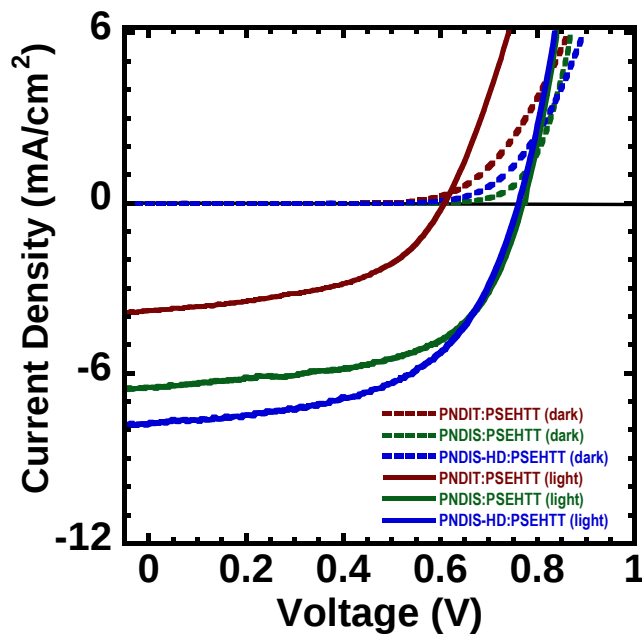


Figure S10. (a) Current density (J) – voltage (V) characteristics of all-polymer BHJ solar cells from 1:1 wt/wt blend each of PSEHTT:PNDIT, PSEHTT:PNDIS, and PSEHTT:PNDIS-HD under illumination with the corresponding dark current density.

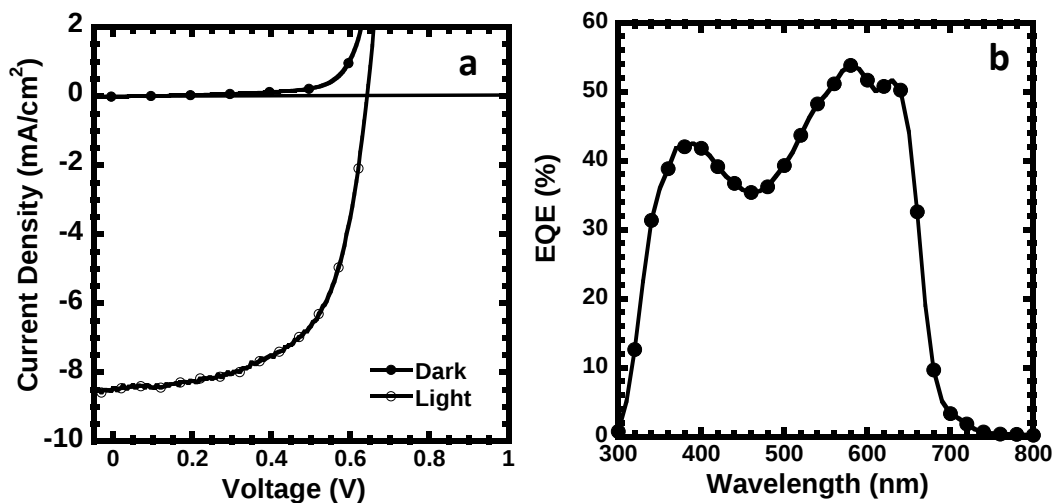


Figure S11. (a) Current density (J) - voltage (V) characteristics and (b) EQE spectrum of PSEHTT:PC₆₀BM solar cells. Device structure: ITO/ZnO/PSEHTT:PC₆₀BM/MoO₃/Ag.

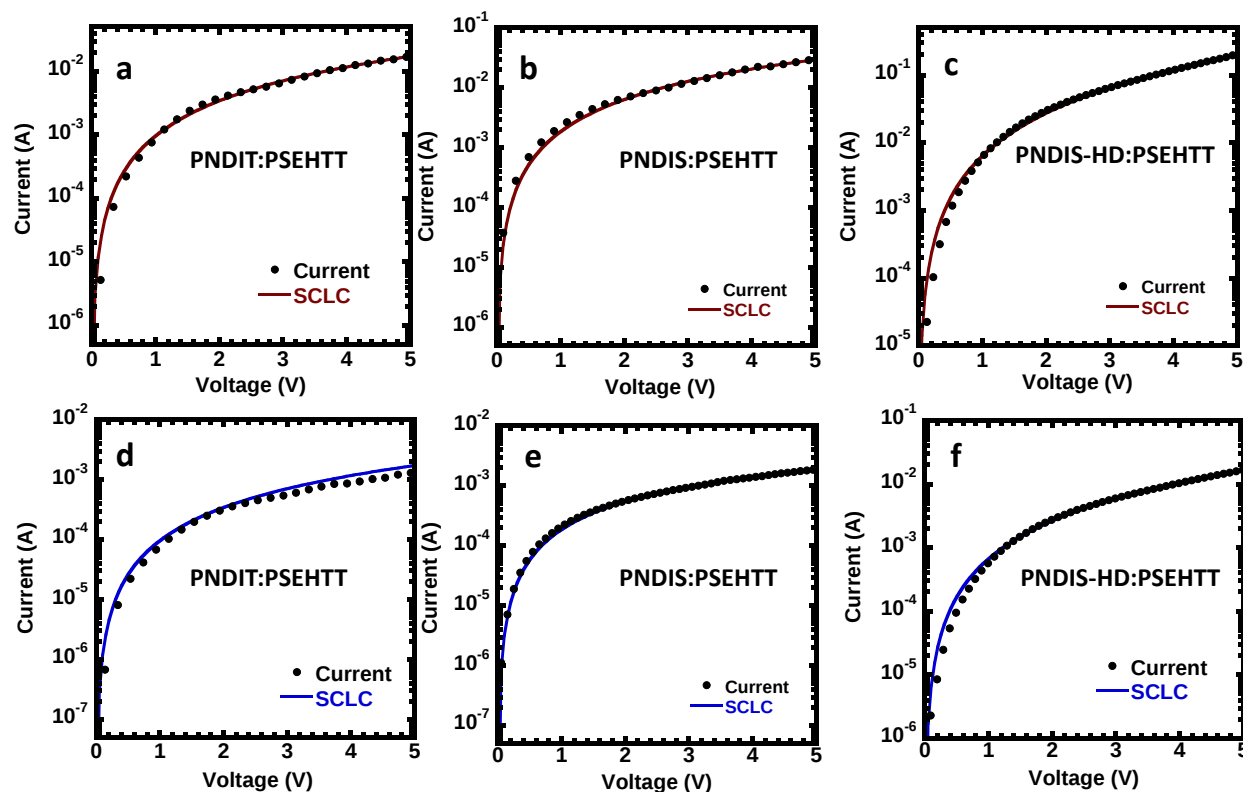


Figure S12. Current (I) -voltage (V) characteristics and space-charge-limited current (SCLC) fittings of devices measured in ambient conditions. Hole-only SCLC devices: ITO/PEDOT:PSS/blend/Au with (a) PNDIT:PSEHTT=1:1, (b) PNDIS:PSEHTT=1:1, and (c) PNDIS-HD:PSEHTT=1:1 blends; Electron-only SCLC devices: ITO/ZnO/blend/LiF/Al with (d) PNDIT:PSEHTT=1:1, (e) PNDIS:PSEHTT=1:1, and (f) PNDIS-HD:PSEHTT=1:1 blends.

References

- (S1) Sun, Y.; Seo, J. H.; Takacs, C. J.; Seifert, J.; Heeger, A. J. *Adv. Mater.* **2011**, 23, 1679.
 (S2) Murgatroyd, P. N. *J. Phys. D: Appl. Phys.* **1970**, 3, 1488.