

Electronic Supplementary Information (ESI)

Fluro-benzoselenadiazole-based low bandgap polymers for high efficiency organic solar cells

Yong-Xi Li^a, Zhe Pan^a, Lei Miao^{b*}, Ying Xing^a, Chao Li^a, Yu Chen^{a*}

^a *Key Laboratory for Adv. Mater., Institute of Applied Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.*

E-mail: chentangyu@yahoo.com.

^b *Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China; E-mail: miaolei@ms.giec.ac.cn*

Experimentals

General characterization methods: UV/Vis absorption spectra were measured using a Perkin-Elmer Lambda-9 spectrophotometer. The ¹H NMR spectra were collected on a Bruker AV 300 spectrometer operating at 300 MHz in deuterated chloroform solution with TMS as reference, respectively. The molecular weight was measured by a Waters 1515 gel permeation chromatograph with a refractive index detector at room temperature (THF as the eluent). Cyclic voltammetry of polymer films were measured against Ag/Ag⁺ as the reference electrode, ITO as working electrode and Pt mesh electrode in an 0.1 M electrolyte containing tetrabutylammonium hexafluoro-phosphate in acetonitrile with a scan rate of 100 mV/s. MS spectra were recorded on Bruker APEX Qe 47.

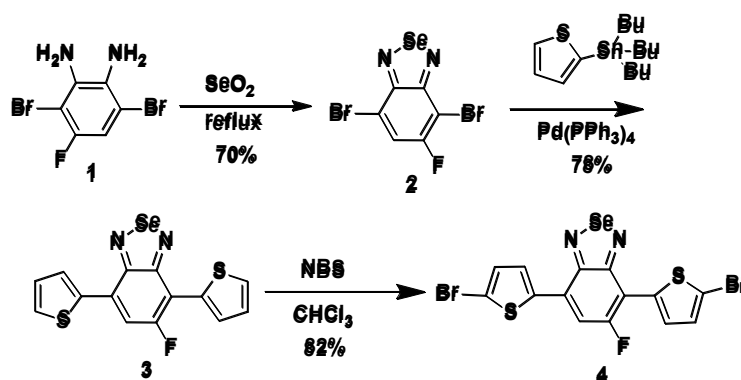
Device Fabrication and Characterization of FET: Field-effect transistors were fabricated through the top-contact and bottom-gate geometry. Heavily doped p-type silicon <100> substrates with a 300 nm thermal oxide layer were purchased from Montco Silicon Technologies INC. After cleaning the substrate by sequential ultrasonication in acetone and isopropyl alcohol for 15 min followed by air plasma treatment, the oxide layer was passivated with a thin divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) buffer layer.

Polymer thin films were spin-coated from a 0.5wt% DCB solution. Interdigitated source and drain electrodes ($W=1000\ \mu\text{m}$, $L=20/30\ \mu\text{m}$) were defined by evaporating aAu (40 nm) through a shadow mask from the resistively heated Mo boat below 2×10^{-6} Torr. OFET characterization was carried out in a N_2 -filled glovebox using an Agilent 4155B semiconductor parameter S6 analyzer. The field-effect mobility was calculated in the saturation regime from the linear fit of $(I_{\text{ds}})_{1/2}$ vs V_{gs} . The threshold voltage (V_t) was estimated as the x intercept of the linear section of the plot of $(I_{\text{ds}})_{1/2}$ vs V_{gs} . The sub threshold swing was calculated by taking the inverse of the slope of I_{ds} vs V_{gs} in the region of exponential current increase.

Device Fabrication and Characterization of PSCs: ITO-coated glass substrates ($15\ \Omega/\text{sq}$) were cleaned with detergent, de-ionized water, acetone, and isopropyl alcohol. A thin layer (ca. 35 nm) of PEDOT:PSS (Baytron® P VP AI 4083, filtered at $0.45\ \mu\text{m}$) was first spin-coated on the pre-cleaned ITO-coated glass substrates at 5,000 rpm and baked at 140°C for 10 minutes under ambient conditions. The substrates were then transferred into an argon-filled glove-box. Subsequently, the polymer : PC₇₁BM active layer (ca. 90 nm) was spin-coated on the PEDOT:PSS layer at 800 rpm from a homogeneously blended solution. The solution was prepared by dissolving the polymer and fullerene at weight ratios of 1:2.5 in o-dichlorobenzene (ODCB) to a total concentration of 20 mg/mL at $80\ ^\circ\text{C}$ overnight and filtered through a PTFE filter ($0.20\ \mu\text{m}$). All of the substrates were placed on the hot plate at 150°C for 10min. After annealing, a 10 nm thick film of C₆₀-bis surfactant (2 mg/mL in methanol) was spin-coated at 5k rpm and annealed at $110\ ^\circ\text{C}$ for 5 min to drive off any remaining solvent prior to metal deposition. At the final stage, the substrates were pumped

down to high vacuum ($< 2 \times 10^{-6}$ Torr), and silver (100 nm) was thermally evaporated onto the active layer. Shadow masks were used to define the active area (10.08×10^{-2} cm²) of the devices.

Materials Synthesis: All chemicals, unless otherwise specified, were purchased from Aldrich and used as received. Compound (4,8-Bis(5-(2-decyltetradecyl)-thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane),¹ 2,7-bis(trimethyltin)-4,9-dihydro-4,9,9-tetradodecyl-sindaceno[1,2-b:5,6-b']-dithiophene,² and 3,6-dibromo-4-fluoro-1,2-phenylenediamine³ were synthesized according to the reported procedures.



Scheme 1

Chemical structures and synthetic routes of monomers 4.

4,7-Dibromo-5-fluoro-2,1,3-benzoselenadiazole (2): To a solution of 3,6-dibromo-4-fluoro-1,2-phenylenediamine (2.8 g, 10 mmol) in refluxing ethanol (50 mL) was added a solution of selenium dioxide (1.19 g, 10 mmol) in hot water (20 mL). The mixture was heated under reflux for 5 h. Filtration of the yellow precipitates and recrystallization from ethyl acetate gave 4,7-dibromo-5-fluoro-2,1,3-benzoselenadiazole (2.5 g) in 70% yield as pale yellow needles. ¹H NMR (300 MHz, d-CDCl₃, ppm): 7.78 (d, J= 9.0 Hz, 1H). ¹³C NMR (125 MHz, d-CDCl₃, ppm): 114.3, 114.1, 106.2, 106.1. ¹⁹F NMR (d-CDCl₃, ppm): -102.11 (d, J=1.25 Hz),

-102.13 (d, $J=1.25$ Hz). MS (m/z): $[M+H]^+$ calcd for $C_6HBr_2FN_2Se$, 359.76; found, 357.2031.

4,7-Dithiophen-2'-yl-5-fluro-2,1,3-benzoselenadiazole(3): 4,7-dibromo-5-fluro-2,1,3-benzothi adiazole (341mg, 1.0mmol) was placed in a tri-necked flask and the flask was subsequently filled with dried nitrogen, then anhydrous THF (50ml) and tributyl(thiophen-2-yl)stannane (1.12g, 3.0 mmol) were added. Then the solution bubble with nitrogen for 30 min. A catalyst $Pd(PPh_3)_2Cl_2$ (14.3mg, 0.02mmol) was added into the mixture and the reaction was allowed to proceed by refluxing the mixture overnight at about $70^\circ C$. After the reaction was completed, the solvent was removed by reduced pressure evaporation, and the crude products were purified by column chromatography (hexane/ $CH_2Cl_2 = 1/1$) obtained red solid (yield: 78%). 1H NMR (300 MHz, $d-CDCl_3$, ppm): 8.15 (d, $J=4.2$ Hz, 1H), 8.05 (d, $J=4.2$ Hz, 1H), 7.78 (d, $J=9.0$ Hz, 1H), 7.58 (d, $J=4.2$ Hz, 1H), 7.53 (d, $J=4.2$ Hz, 1H), 7.23 (d, $J=4.2$ Hz, 1H), 7.21 (d, $J=4.2$ Hz, 1H). ^{19}F NMR ($d-CDCl_3$, ppm): -108.03 (d, $J=1.25$ Hz), -108.05 (d, $J=1.25$ Hz). MS (m/z): $[M+H]^+$ calcd for $C_{14}H_7FN_2S_2Se$, 365.92; found, 365.2302.

4,7-Bis(5'-bromo-2'-thiophenyl)-5-fluro-2,1,3-benzoselenadiazole (4): Compound 3 (280mg, 0.88mmol) and NBS (470mg, 2.64mmol) were dissolved in a stirred mixture of chloroform (30mL) and acetic acid (5mL) under nitrogen. The reaction mixture was stirred at room temperature overnight, then poured into the water, extracted with DCM for three times. the solvent was removed by reduced pressure evaporation, and the crude products were purified by column chromatography (hexane/ $CH_2Cl_2 = 1/1$) obtained red dark solid (yield: 82%). 1H NMR (300 MHz, $d-CDCl_3$, ppm): 7.92 (d, $J=4.2$ Hz, 1H), 7.72 (d, $J=4.2$ Hz, 1H), 7.71 (d, $J=9.0$

Hz,1H),7.20 (d, J=4.2 Hz,1H),7.18 (d, J=4.2 Hz,1H)..MS (m/z): [M+H]⁺calcd for C₁₄H₅Br₂FN₂S₂Se, 523.74; found, 525.4764.

General method of microwave-assisted polymerization by Stille coupling. In a 10 mL microwave tube was charged with di-tin monomer (0.5 mmol) and the compound 4 (0.48 mmol) in a mixture of o-xylenes (2 mL) and DMF (0.2 mL). After being purged with argon for 15 min. Pd₂(dba)₃ (0.024 mmol) and P(o-tol)₃ (0.087 mmol) were added consequently. Then, the resulted mixture was heated in a microwave reactor at 120 °C for 5 min, 150 °C for 5 min, and 170 °C for 40 min. After cooling to room temperature, the resulted mixture was precipitated by adding into methanol (50 mL) and filtered. The collected precipitate was subjected to Soxhlet extraction with methanol, hexanes, and chloroform. The high molecular weight part was collected and dried under vacuum. The yield and results of the polymers are as follows:

PBDT-T-FBSe: ¹H NMR (300 MHz,d-CDCl₃, ppm): 8.10–6.91 (br, 11H), 2.91 (br, 4H), 1.74–1.22 (br, 82H), 0.88 (br, 12H).Molecular weight: M_n = 27.6kDa, M_w= 59.1 kDa, PDI = 2.14. yield 64%.

PIDT-T-FBSe:¹H NMR (300 MHz,d-CDCl₃, ppm): 8.12 (s, 2H), 7.98 (s, 2H), 7.94(br, 1H), 7.80(br, 1H),7.76(br, 1H), 7.28 (br, 1H),7.24(br, 1H), 2.0-1.9 (br, 8H), 1.20-1.14 (br, 72H), 0.86-0.81 (br, 20H). Molecular weight: M_n = 32.2 kDa, M_w= 76.3 kDa, PDI = 2.37. yield 71%.

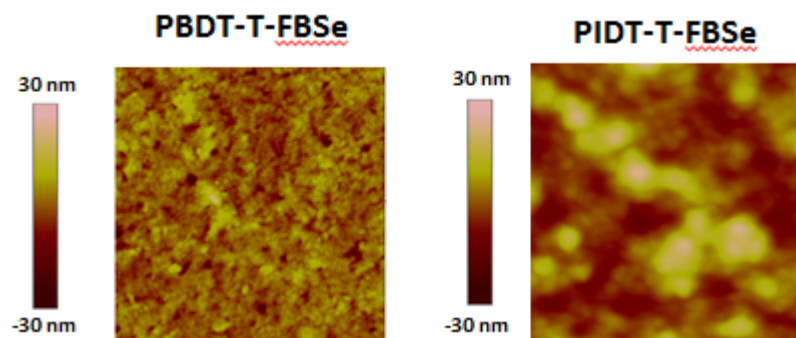


Figure S1. AFM topography images of polymers:PC₇₁BM(1 : 2.5wt) blend films from o-DCB solutions.

References:

1. Y. Liu, H. Wang, H. Dong, J. Tan, W. Hu and X. Zhan, *Macromolecules*, 2012, **45**, 1296-1302.
2. M. Zhang, X. Guo, X. Wang, H. Wang and Y. Li, *Chemistry of Materials*, 2011, **23**, 4264-4270.
3. Y. Zhang, S.-C. Chien, K.-S. Chen, H.-L. Yip, Y. Sun, J. A. Davies, F.-C. Chen and A. K. Y. Jen, *Chemical Communications*, 2011, **47**, 11026-11028.