Electronic Supporting Information (ESI) for:

Positional Effects of Alkyl Chain on Photovoltaic Performances of Quinoxaline-Based Polymers

Dinda Fariesta Nugraha,^{a†} Yifan Yu,^{b†} Jung Won Yoon,^b Hyungju Ahn,^c Juan Anthony

Prayogo,^a Dong Ryeol Whang,^d Jihoon Lee,^{*b} Hyosung Choi,^{*b} and Dong Wook Chang^{*a}

^aDepartment of Industrial Chemistry and CECS Research Institute, Pukyong National University, 48513 Busan, Republic of Korea

^bDepartment of Chemistry, Research Institute for Natural Science and Institute of Nano Science and Technology, Hanyang University, 04730 Seoul, Republic of Korea ^cPohang Accelerator Laboratory, POSTECH, Pohang 37673, Republic of Korea. ^dDepartment of Advanced Materials, Hannam University, 34054 Daejeon, Republic of Korea

E-mail: jhlee227@hanyang.ac.kr, hschoi202@hanyang.ac.kr, and dwchang@pknu.ac.kr

[†]D. F. Nugraha and Y. Yu equally contributed equally

1. Experimental section

1.1 Materials and Instruments

4,7-dibromobenzo[c][1,2,5]thiadiazole-5-carbonitrile (1),^{S1} 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5-carbonitrile (5),^{S2} 1,2-bis(5-(2-butyloctyl)thiophen-2-yl)ethane-1,2-dione (6),^{S3} tributyl(4-(2-butyloctyl)thiophen-2-yl)stannane ^{S4} and 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-

diyl)bis(trimethylstannane (8)^{S5} were prepared according to previous reports. Other chemicals and solvents, were purchased from Sigma-Aldrich Co., Inc. and directly used without further purification. The analysis for ¹H and ¹³C nuclear magnetic resonance (NMR) were carried out using JEOL JNM-ECZ-400 NMR spectrometer. UV-Visible spectra were analyzed with Perkin Elmer UV-Vis Lambda 365 Spectrometer, while the measurement of Cyclic Voltammetry (CV) was done using VersaSTAT 3 Potentiometry (Princeton Applied Research) with 0.1 M of tetrabutylammonium hexafluorophosphate (TBAP) in acetonitrile as electrolyte. The utilized working, reference, and counter electrodes were glassy carbon electrode coated with polymers, Ag wire, and Pt wire, sequentially. Ferrocene/ferrocenium was employed as external standard for CV measurement. Gel Permeation Chromatography (GPC) analysis was performed using Agilent 1200 series instrument with tetrahydrofuran as the solvent.

1.2. Fabrication and characterization of photovoltaic device

1.2.1. Fabrication of PSCs

The glass substrates with indium tin oxide (ITO) are sequentially cleaned with deionized water, acetone, and isopropyl alcohol, and each step is treated with ultrasound for 15 minutes. The substrates were dried in an oven and then irradiated with UV ozone for 20 minutes. For PSCs, Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was spin-coated onto ITO glass and then annealed at 140 °C for 10 min. The active layer mixture of

donor:Y6 (1:1.2 w/w) was dissolved in chloroform (CF) and 0.4 vol% of 1,8-diiodooctane (DIO) was added as an additive. All active layer mixture with 12 mg/mL concentrations were stirred at 50 °C for about 4 h. The active layer was spin-coated on the hole transport layer and then annealed at 110 °C for 10 min. After spin-coating 3,3'-(1,3,8,10-Tetraoxoanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(N,N-dimethylpropan-1-amine oxide) (PDINO) as an electron transport layer on the active layer, finally the aluminum 120 nm for a metal electrode was thermally evaporated.

1.2.2. Photovoltaic characterization of PSCs

The photovoltaic performances were evaluated using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 mW cm⁻². The current density-voltage (*J-V*) curves were recorded using an LCS-100 series small area solar simulator (Keithley 2400). The external quantum efficiency (EQE) spectra were measured using a Newport Oriel QuantX300 equipped with an Oriel Cornerstone 130 monochromator.

1.2.3. Measurements of charge mobility

The electron and hole mobilities were measured using the space charge-limited current (SCLC) method. For the measurements, pure electron and pure hole devices with ITO/zinc oxide (ZnO)/active layer/PDINO/A1 and ITO/PEDOT:PSS/active layer/Au structures were utilized. The charge mobility was determined by fitting the dark current to a model of a single carrier SCLC described by the Mott-Gurney law:

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

Here, J represents the current density, ε_0 is the dielectric constant in free space (8.85419×10⁻¹² C V⁻¹ m⁻¹), ε_r is the relative dielectric constant of the material, μ denotes the

mobility of the charge carrier, V is the applied voltage, and L indicates the thickness of the film. The mobility of the charge carrier was calculated from the slope of the J-V curve.

1.2.4. Measurements for molecular orientations

GIWAXS measurements. The grazing incidence wide-angle X-ray scattering (GIWAXS) data were collected using synchrotron radiation at the Pohang Accelerator Laboratory (PAL) in the Republic of Korea.

AFM topology. The morphology images were obtained by non-contact detection mode of atomic force microscope (AFM) with a XE-100 (Park Systems).



Scheme S1. Synthesis of the monomers and polymers

1.3. Syntheses

1.3.1. Synthesis of 4,7-bis(4-(2-butyloctyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5carbonitrile (2)

4,7-dibromobenzo[c][1,2,5]thiadiazole-5-carbonitrile (1, 2.50 mmol), tributyl(4-(2-butyloctyl)thiophen-2-yl)stannane (5.50 mmol) and Pd(P(Ph₂)Cl₂) (5 mol%) were dissolved in toluene (30 mL). After N₂ has been bubbled for 15 min, the mixture was refluxed for 24 h under a N₂ atmosphere. Once the reaction was completed, the mixture was cooled to room temperature and filtered with celite. After removal of the solvent, the residue was purified by column chromatography with dichloromethane/hexane (1/4, v/v). Yield = 88%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.99 (s, 1H), 7.94 (d, 2H), 7.27-7.26 (d, 1H), 7.09-7.08 (d, 1H), 2.66-2.61 (q, 4H), 1.76-1.62 (br, 2H), 1.30-1.24 (t, 32H), 0.90-0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 153.15, 143.50, 142.74, 136.86, 134.03, 133.10, 130.73, 127.39, 126.99, 126.92, 124.21, 119.08, 109.06, 39.06, 39.00, 35.09, 34.90, 33.40, 33.09, 33.07, 32.01, 29.80, 28.98, 26.72, 26.69, 23.17, 22.79, 14.27, 14.23.

1.3.2. Synthesisof4,7-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5-carbonitrile (3)

A mixture of **1** (0.90 mmol) and *N*-bromosuccinimide (2.20 mmol) in tetrahydrofuran (30 mL) was stirred at room temperature for 12 h. The solution was poured into water and extracted with ethyl acetate. The organic layer was dried over MgSO₄ and filtered. The solvents were removed by using rotary evaporator and the residue was purified with column chromatography with dichloromethane/hexane (1/4, v/v). Yield = 92%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.90-7.88 (d, 2H), 7.72 (s, 1H), 2.60-2.56 (q, 4H), 1.81-1.68 (br, 2H), 1.31-1.26 (d, 32H), 0.90-0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 152.76, 152.68, 142.77, 142.22,

136.34, 133.91, 132.50, 129.78, 126.95, 126.12, 118.81, 117.35, 114.37, 108.44, 38.68, 34.34, 34.25, 33.43, 33.13, 31.99, 29.78, 28.89, 26.64, 23.16, 22.78, 14.23.

1.3.3. Synthesis of 5,8-bis(5-bromo-4-(2-butyloctyl)thiophen-2-yl)-2,3-di(thiophen-2-yl)quinoxaline-6-carbonitrile (4)

A mixture of 3 (1.10 mmol) and zinc powder (22 mmol) in acetic acid (20 mL) was refluxed for 3h. Once the reaction was completed, the mixture was filtered and the filtrate was collected. 2,2'-Thenil (1.10 mmol) was added to the filtrate and stirred overnight at reflux. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic layer was dried over MgSO₄ and filtered. The solvents were removed by using rotary the residue was purified with column chromatography with evaporator and dichloromethane/hexane (1/4, v/v) as the eluent. Yield = 76%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.13 (s, 1H), 7.74 (s, 1H), 7.64-7.62 (dd, 1H), 7.61-7.59 (dd, 1H), 7.57-7.57 (dd, 1H), 7.55-7.54 (dd, 1H), 7.50 (s, 1H), 7.08-7.05 (m, 2H), 2.60-2.56 (q, 4H), 1.82-1.70 (br, 2H), 1.32-1.26 (m, 32H), 0.90-0.84 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 146.69, 146.29, 141.24, 141.05, 140.84, 140.81, 137.50, 136.75, 135.50, 134.19, 133.21, 131.97, 131.39, 131.21, 131.03, 130.81, 128.90, 128.45, 127.94, 127.78, 119.29, 117.66, 116.27, 109.80, 38.79, 38.75, 34.34, 34.29, 33.48, 34.29, 33.48, 33.18, 32.02, 29.80, 28.93, 26.67, 23.18, 22.78, 14.27, 14.24, 1.13. HRMS-EI m/z: [M⁺] calcd. for C₄₉H₅₉Br₂N₃S₄, 997.1938; found, 997.1946.

1.3.4. Synthesis of 5,8-bis(5-bromothiophen-2-yl)-2,3-bis(5-(2-butyloctyl)thiophen-2yl)quinoxaline-6-carbonitrile (7)

A mixture of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole-5-carbonitrile (5, 1.10 mmol) and zinc powder (22 mmol) in acetic acid (20 mL) was refluxed for 3h. Once the reaction was completed, the mixture was filtered and the filtrate was collected. 1,2-Bis(5-(2-

butyloctyl)thiophen-2-yl)ethane-1,2-dione (**6**, 1.10 mmol) was added to the filtrate and stirred overnight at reflux. After cooling to room temperature, the mixture was poured into water and extracted with ethyl acetate. The organic layer was dried over MgSO₄ and filtered. The solvents were removed by using rotary evaporator and the residue was purified with column chromatography with dichloromethane/hexane (1/2, v/v) as the eluent. Yield = 47%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.11 (s, 1H), 7.81-7.80 (d, 1H), 7.55-7.54 (d, 1H), 7.51-7.50 (d, 1H), 7.47-7.46 (d, 1H), 7.19-7.18 (d, 1H), 7.15-7.14 (d, 1H), 6.73-6.70 (q, 2H), 2.86-2.82 (q, 4H), 1.79-1.56 (br, 2H), 1.34-1.24 (m, 32H), 0.91-0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 152.15, 151.58, 146.89, 146.52, 136.39, 137.77, 137.20, 136.35, 135.45, 133.97, 131.51, 130.98, 130.90, 130.57, 129.56, 129.44, 128.49, 126.86, 126.31, 126.11, 119.63, 119.33, 118.38, 109.29, 40.07, 35.02, 34.98, 33.45, 33.07, 32.00, 29.73, 28.97, 26.64, 23.08, 22.79, 14.27, 14.24. HRMS-EI m/z: [M⁺] calcd. for C₄₉H₅₉Br₂N₃S₄, 997.1938; found, 997.1952.

General polymerization procedure under Stille coupling condition

In a Schlenk flask, 4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane (**8**, 0.2 mmol), dibrominated quinoxaline monomer (0.2 mmol), $Pd_2(dba)_3$ (10% mol) and tri(o-tolyl)phosphine (40% mol) were dissolved in the mixture of dry chlorobenzene and dimethylformamide (4/1, v/v). After N₂ bubbling for 15 min, the mixture was stirred at 110 °C for 48 h under N₂ protection. At the end of polymerization process, end-capping agents of 2-tributylstannylthiophene and 2-bromothiophene were sequentially added within an interval of 2 h. Once the polymerization was completed, the mixture was further purified via Soxhlet extraction with methanol, acetone, hexane, and chloroform. The final chloroform fraction was collected and concentrated.

After precipitation of the polymers using methanol, the final polymer powder was filtered and dried in vacuum oven at 60 °C.

1.3.5. Synthesis of **PBT-TdQxCN**

8 and **4** were used as monomers. Yield = 75%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.75-7.44 (br, 9H), 7.23-6.92 (br, 4H), 2.97-2.77 (br, 8H), 1.83-1.69 (br, 6H), 1.33-0.87 (br, 76H). Molecular weight (GPC): $M_n = 16.37$ kDa and polydispersity index (PDI) = 1.49. Elemental analysis: calcd (%) for C₈₅H₁₀₃F₂N₃S₈: C 69.87, H 7.11, N 2.88; found: C 69.90, H 7.21, N 3.04.

1.3.6. Synthesis of PBT-TuQxCN

8 and **7** were used as monomers. Yield = 80%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.12-7.27 (br, 9H), 7.17-6.70 (br, 4H), 3.08-2.60 (br, 8H), 1.93-1.65 (br, 6H), 1.40-0.88 (br, 76H). Molecular weight (GPC): M_n = 16.11 kDa and polydispersity index (PDI) = 2.77. Elemental analysis: calcd (%) for C₈₅H₁₀₃F₂N₃S₈: C 69.87, H 7.11, N 2.88; found: C 69.91, H 7.05, N 2.98.



Fig. S1. (a) Simulated UV-vis absorption spectra, (b) related absorption characteristics, and (c) detailed molecular orbitals of PBT-dQxCN and PBT-uQxCN.



Figure S2. SCLC characteristics of the polymers for (a) hole mobility and (b) electron mobility.

	In-plane		Out-of-plane	
	q _{xy} (Å ⁻¹)	d ₍₁₀₀₎ (Å)	q _z (Å-1)	$\mathbf{d}_{(\pi-\pi)}(\mathrm{\AA})$
PBT-dQxCN	0.31	20.00	1.53	4.19
PBT-uQxCN	0.27	23.59	1.65	3.80
PBT-dQxCN:Y6	0.29	21.81	1.71	3.65
PBT-uQxCN:Y6	0.27	23.24	1.71	3.67

Table S1. Summary of GIWAXS parameters of pristine films and blends.

Reference

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<Appendix- ¹H and ¹³C NMR spectra>









