Supporting Information

Benzo[1,2,5]thiadiazole 기반 비융합형 비풀러렌 단분자 전자 수용체의 플루오린화가 고분자 태양전지 성능에 미치는 영향

박경헌 [a,#] 송창은,[b,c,#] 피자 아르샤드,[b,c] 임은희 [a,*]

[a] 서울시립대학교 융합응용화학과, [b] 한국화학연구원, [c] 과학기술연합대학원대학교

Effect of Fluorination of Benzo[1,2,5]thiadiazole-Based Nonfused Nonfullerene Small Molecular Acceptors on Polymer Solar Cell Performance

Kyoungheon Park,[a,#] Chang Eun Song,[b,c,#] Fiza Arshad,[b,c] and Eunhee Lim[a,*]

[a] Department of Applied Chemistry, University of Seoul, 163 Seoulsiripdae-ro, Dongdaemun-gu, Seoul 02504, Republic of Korea

[b] Korea Research Institute of Chemical Technology (KRICT), 141 Gajeongro, Yuseong-gu, Daejeon 34114, Republic of Korea

[c] Advanced Materials and Chemical Engineering, University of Science and Technology (UST), Daejeon 34113, Republic of Korea

# K. Park and C. E. Song contributed equally to this work.

* Corresponding author: Tel. +82-2-6490-2465; E-mail address: ehlim@uos.ac.kr (E. Lim)

S1. Materials and measurement

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxaldehyde (B-T-CHO) and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) were purchased from Tokyo Chemical Industry (Tokyo, Japan). Piperidine, tri-*tert*-butylphosphonium tetrafluoroborate ($P(t\text{-}Bu)_3 \cdot HBF_4$), potassium phosphate tribasic (K_3PO_4), and 4,7-dibromobenzo[*c*]-1,2,5-thiadiazole were purchased from Sigma-Aldrich (Gyeonggi-do, Korea). 4,7-Dibromo-5,6-difluoro-2,1,3-benzothiadiazole was purchased from Combi-Blocks (Gyeonggi-do, Korea). 4,7-Diiodo-5-fluorobenzo[c][1,2,5]thiadiazole was synthesized following a reported procedure.[S1] All chemicals were used as received without further purification, and all reactions were carried out under a nitrogen atmosphere with anhydrous solvents. 3-Octylrhodanine (ORH) was synthesized according to our previous report.[S2]

^1H-NMR spectra were recorded using a Bruker AVANCE III HD400 spectrometer (Bruker, Germany). The ^{13}C NMR spectrum of **T-BT-T-ORH** was obtained using a Bruker AVANCE III 500 spectrometer (Bruker, Germany). The ^{13}C NMR spectra of **T-1FBT-T-ORH** and **T-2FBT-T-ORH** were recorded using a Bruker AVANCE III HD800 instrument (Bruker, Germany) installed at the Korea Basic Science Institute (KBSI), Ochang Center. Elemental analysis (EA) was performed on the solid samples using a Vario Micro Cube elemental analyzer at the KBSI Pusan Center. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using a TGA/DSC 1 and a DSC 1 (Mettler-Toledo, Switzerland), respectively, under a nitrogen atmosphere at a heating/cooling rate of 10°C min^{-1}. UV–vis spectra were recorded using a Mega-U600 spectrophotometer (Scinco, Korea). Solution samples were prepared by dissolving the analytes in chloroform (5 ppm), and thin-film samples were prepared by spin-coating onto glass substrates. Optical bandgaps ($E_{g,opt}$)

were estimated from the absorption onset wavelengths ($E_{g,opt} = 1240/\lambda_{onset}$ (eV)). Cyclic voltammetry (CV) was performed using a BAS 100B electrochemical analyzer (Bioanalytical Systems Inc., USA), calibrated with a ferrocene/ferrocenium (Fc/Fc^+) reference (−4.8 eV). A three-electrode system was employed, consisting of a nonaqueous reference electrode (0.1 M Ag/Ag^+ in acetonitrile), platinum wire counter electrode, and platinum working electrode. Measurements were conducted in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate at a scan rate of 100 mV s^{-1}.

S2. Device fabrication

The polymer solar cells (PSCs) were fabricated with an inverted structure of indium tin oxide (ITO)/ZnO nanoparticles (NPs)/PEIE/photoactive layer/MoO_x/Ag. The ITO-coated glass substrates were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol (15 min each), and dried in an oven for 5 h. The substrates were then treated in a UV-ozone chamber for 15 min. The polyethylenimine, 80% ethoxylated (PEIE) solution was spin-coated onto the ZnO NP layers, and the ZnO NP/PEIE-coated substrates were subsequently transferred to a nitrogen-filled glove box.

The photoactive layer consisted of the NFSM acceptor developed in this study and a low-bandgap polymer donor of PTB7-Th. The bulk heterojunction active layer was spin-cast at 3000 rpm from a chloroform solution containing the donor and acceptor (15 mg mL^{-1} total concentration) with a fixed donor-to-acceptor ratio of 1:2. Finally, MoO_x (10 nm) and Ag (100 nm) were sequentially deposited via thermal evaporation to complete the inverted device structure.

The current density–voltage (J–V) characteristics were measured using a computer-controlled

Keithley 236 source-measure unit (Keithley Instruments). Device characterization was performed in air under simulated AM 1.5G 100 mW cm^{-2} using a xenon-lamp-based solar simulator (Newport Company). The simulator irradiance was calibrated using a spectrometer, and the illumination intensity was adjusted using an NREL-certified silicon diode with a KG1 optical filter.

The external quantum efficiency (EQE) was recorded using a reflective microscope objective to focus light from a 100 W halogen lamp coupled with a monochromator and optical chopper (PV Measurements, Inc.). The photocurrent was measured using a lock-in amplifier, and the absolute photon flux was determined using a calibrated silicon photodiode.

S3. NMR Spectra

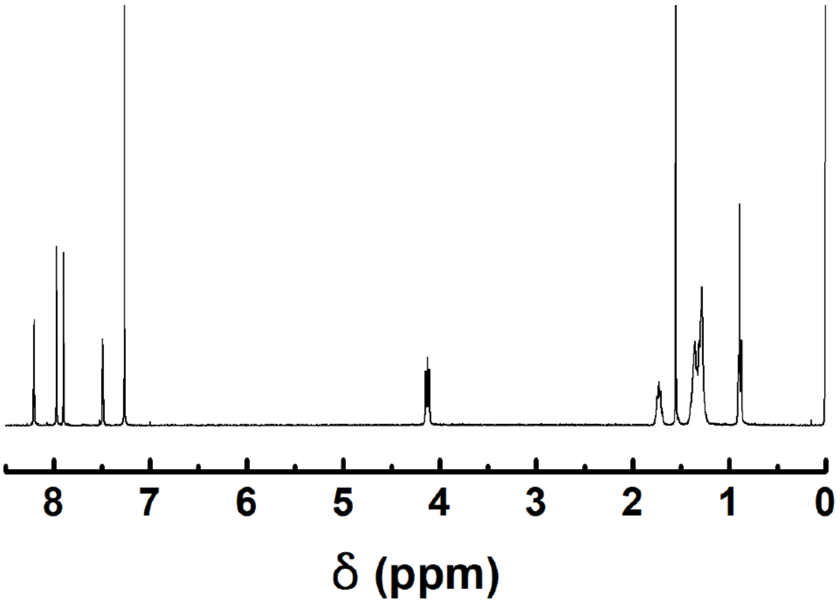

Figure S1. ^{1}H NMR spectrum of **T-BT-T-ORH.**

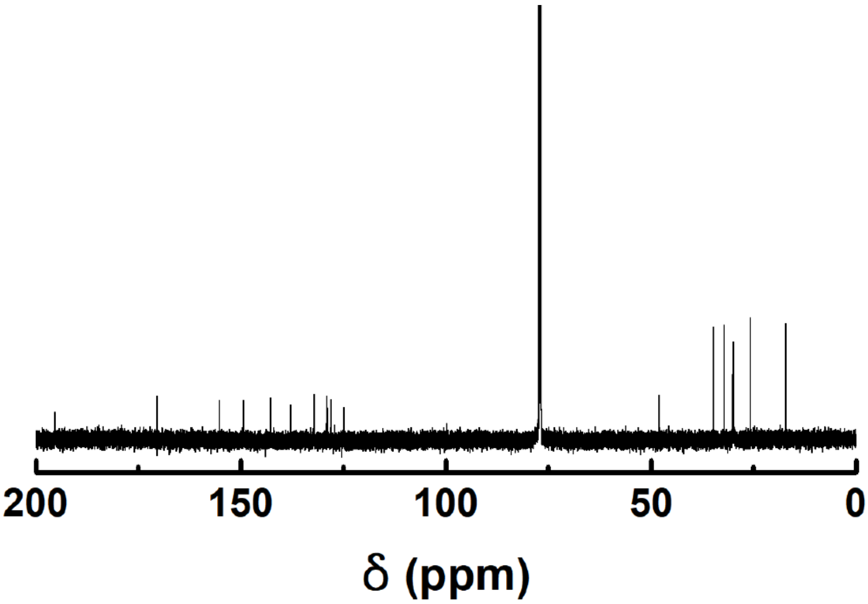

Figure S2. ^{13}C NMR spectrum of **T-BT-T-ORH.**

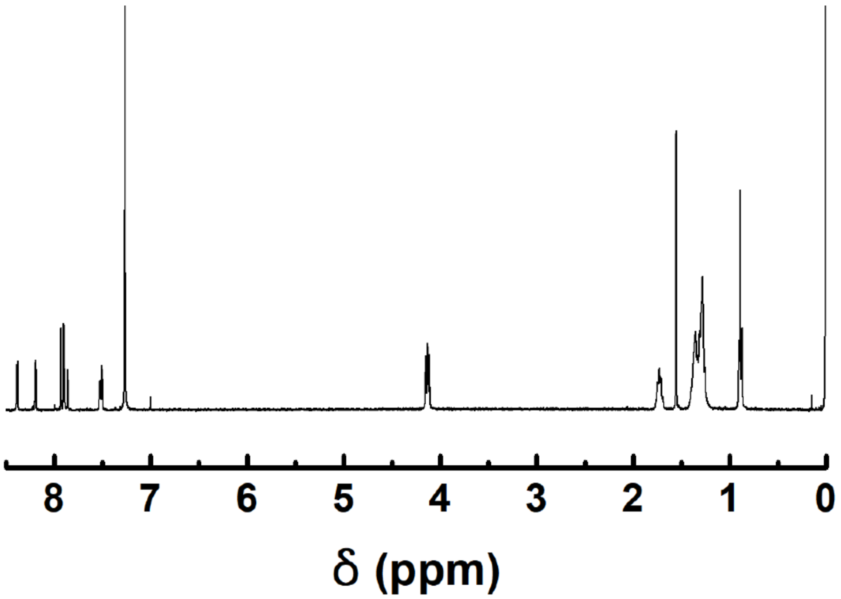

Figure S3. ^{1}H NMR spectrum of **T-1FBT-T-ORH.**

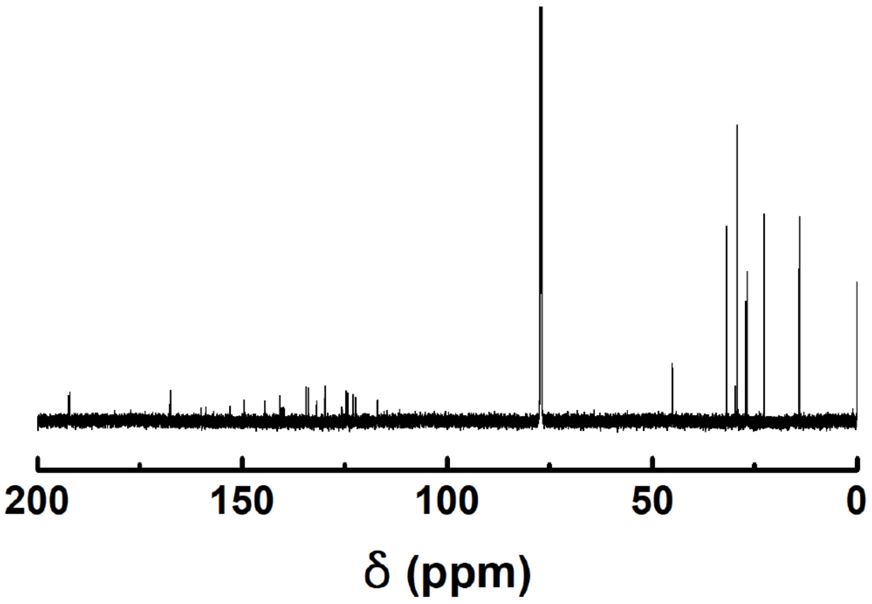

Figure S4. ^{13}C NMR spectrum of **T-1FBT-T-ORH.**

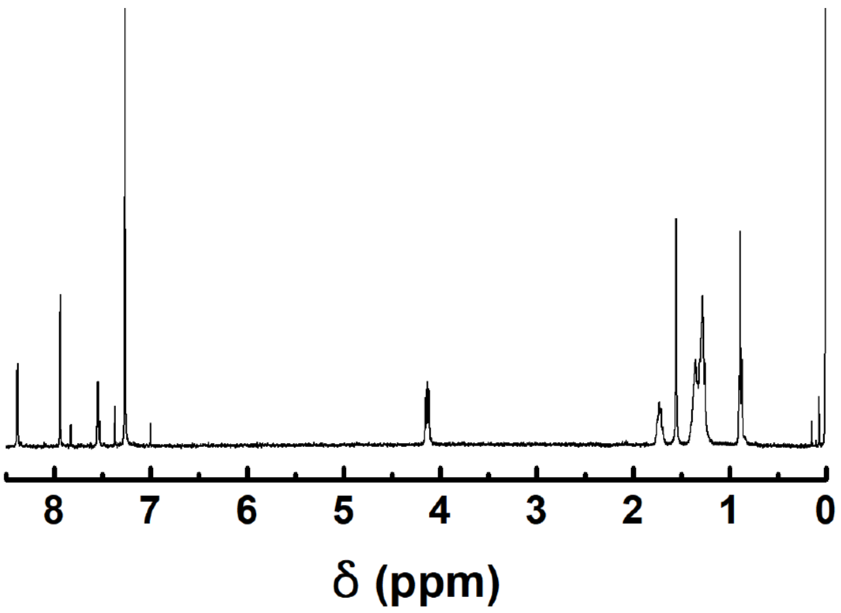

Figure S5. ^{1}H NMR spectrum of **T-2FBT-T-ORH.**

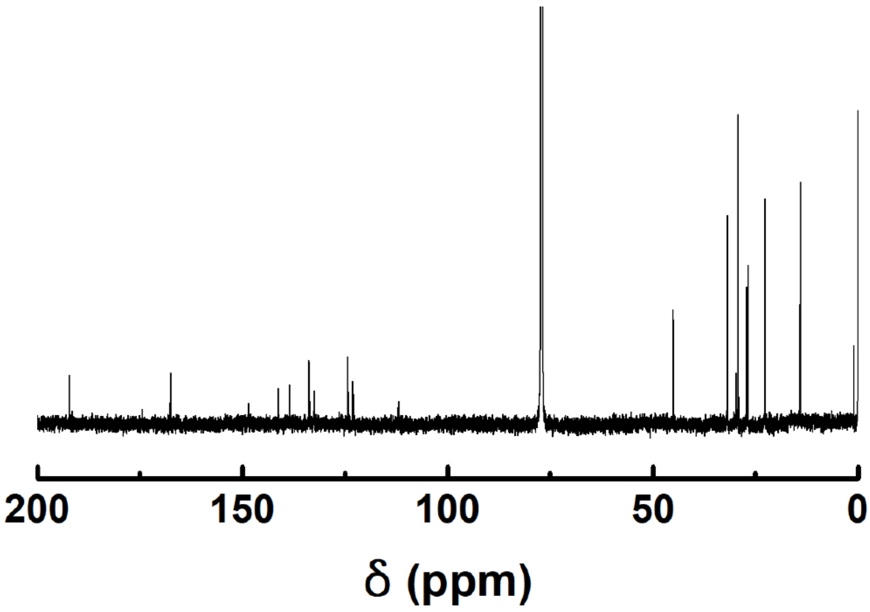

Figure S6. ^{13}C NMR spectrum of **T-2FBT-T-ORH.**

S4. Physical properties

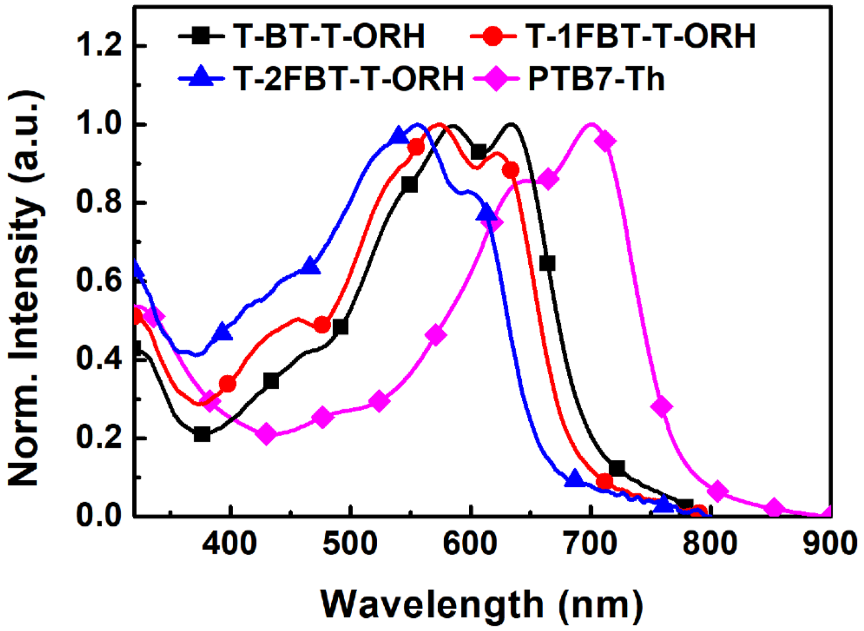

Figure S7. UV–vis absorption spectra of the small molecules and PTB7-Th in films.

S5. PSC properties

Table S1. Detailed device performances of PTB7-Th:acceptor devices

Acceptors	**Annealing** [a]	V_{OC} [V]	J_{SC} [mA cm^{-2}]	***FF*** [%]	**PCE** [%]
T-BT-T-ORH	As-cast	0.93	12.51	41	4.75
	TA (90°C)	1.00	12.73	49	6.27
	TA (120°C)	1.02	10.57	50	5.36
	SVA (CF)	0.97	13.40	51	6.64
	SVA (THF)	0.96	14.49	50	6.92
	SVA (DCM)	0.95	14.28	48	6.47
T-1FBT-T-ORH	As-cast	0.91	11.41	39	3.99
	TA (90°C)	0.94	13.25	47	5.89
	TA (120°C)	0.95	12.22	50	5.78
	SVA (CF)	0.90	12.80	45	5.24
	SVA (THF)	0.92	13.68	46	5.78
	SVA (DCM)	0.92	13.39	45	5.52
T-2FBT-T-ORH	As-cast	0.92	6.70	36	2.25
	TA (90°C)	0.81	6.08	40	1.97
	TA (120°C)	0.72	4.72	40	1.37
	SVA (CF)	0.88	6.93	41	2.47
	SVA (THF)	0.83	7.14	40	2.40
	SVA (DCM)	0.86	6.98	40	2.41

[a] The solvent (CF: chloroform, THF: tetrahydrofuran, DCM: dichloromethane) used for SVA and the annealing temperature for TA are shown in parentheses.

Table S2. V_{OC} and the calculated E_{loss} of the optimized PTB7-Th:acceptor devices[a]

Acceptors	V_{OC} [V]	$E_{g,opt}$ **(donor)** [eV]	$E_{g,opt}$ **(acceptor)** [eV]	E_{loss} [eV]
T-BT-T-ORH	0.96	1.58	1.79	0.62
T-1FBT-T-ORH	0.92	1.58	1.81	0.66
T-2FBT-T-ORH	0.88	1.58	1.90	0.70

[a] E_{loss} is defined ad $E_{loss} = E_g - qV_{OC}$, where E_g is the lowest $E_{g,opt}$ of the donor or acceptor component.

S6. References

(S1) Lin, Y.; Zhang, Z.-G.; Bai, H.; Wang, J.; Yao, Y.; Li, Y.; Zhu, D.; Zhan, X. High-performance fullerene-free polymer solar cells with 6.31% efficiency. *Energ. Environm. Sci.***2015**, 8, 610-616.

(S2) Lee, T.; Eom, Y.; Song, C. E.; Jung, I. H.; Kim, D.; Lee, S. K.; Shin, W. S.; Lim, E. Simple Bithiophene–Rhodanine-Based Small Molecule Acceptor for Use in Additive-Free Nonfullerene OPVs with Low Energy Loss of 0.51 eV. *Adv. Energ. Mater.* **2019**, 9, 1804021.