## Supporting Information

# 퓨란가지는 비대칭 비풀러렌계 어셉터를 기반으로 하는 고분자 태양전지

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# Polymer solar cells based on a furan-containing asymmetric nonfullerene acceptor

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## 1. Synthesis and NMR spectra

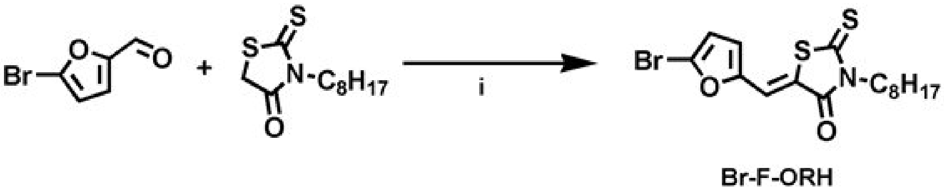
### *1.1 Materials*

Piperidine, potassium phosphate tribasic ($K_3PO_4$), and tri-*tert*-butylphosphonium tetrafluoroborate ($P(t\text{-}Bu)_3 \cdot HBF_4$) were purchased from Sigma-Aldrich (Gyonggi-do, Korea). Chloroform and tetrahydrofuran (THF) were purchased from Alfa Aesar (Seoul, Korea). 5-Bromo-2-furaldehyde and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) were purchased from Tokyo Chemical Industry (Tokyo, Japan). PTB7-Th was purchased from 1 Materials (Dorval, Canada). THF was distilled from sodium and benzophenone under an $N_2$ atmosphere before use.

### *1.2. Synthesis*

The syntheses of octylrhodanine (ORH) and B-T-ORH were described in our previous literatures.[S1,S2] Br-F-ORH and **TF-ORH** were synthesized *via* Knoevenagel condensation and Suzuki coupling reaction, respectively.

*1.2.1. Synthesis of Br-F-ORH.*



5-Bromo-2-furaldehyde (0.84 g, 4.8 mmol) was dissolved in anhydrous chloroform (30 mL), and a few drops of piperidine and ORH (2.94 g, 12.0 mmol) were added. After refluxed and stirred for 5 minute under an $N_2$ atmosphere, the reaction mixture was extracted with dichloromethane, washed with water, and dried over $MgSO_4$. After purification by column chromatography (dichloromethane:hexane = 1:1), the compound Br-F-ORH was obtained as a yellow solid (1.39 g, 72% yield).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.35 (s, 1H), 6.76 (d, $J$ = 3.6 Hz, 1H), 6.52 (d, $J$ = 3.6, 1H), 4.09 (t, $J$ = 7.7 Hz, 2H), 1.69 (m, 2H), 1.27 (m, 10H), 0.88 (t, $J$ = 6.9 Hz, 3H).

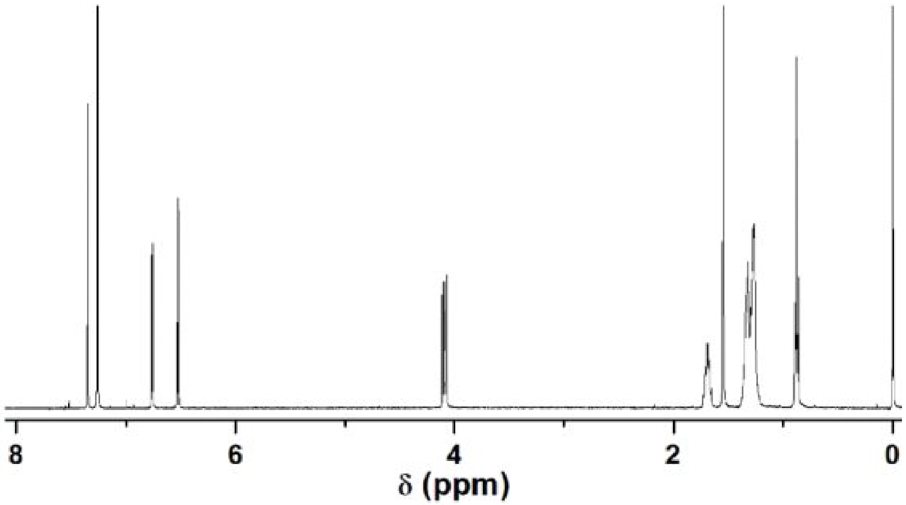
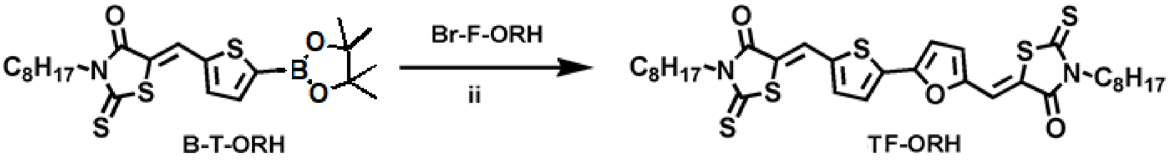


**Figure S1.** $^1$H NMR spectrum of the **Br-F-ORH**.

1.2.2. *Synthesis of TF-ORH.*

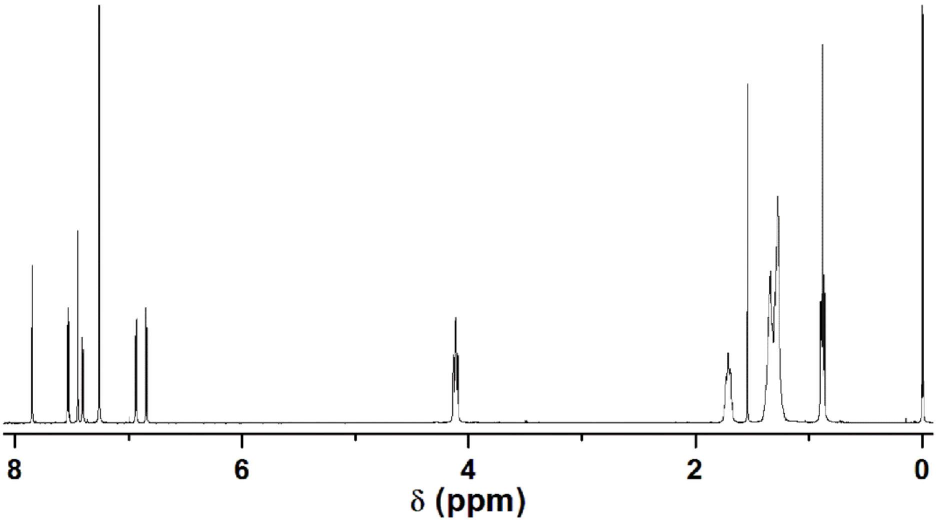


Degassed $H_2O$ solution of $K_3PO_4$ (1 M, 7.2 mL) was added to 30 mL of THF solution of Br-F-ORH (0.95 g, 2.36 mmol), B-T-ORH (1.10 g, 2.36 mmol), P(*t*-Bu)$_3$·$HBF_4$ (0.041 g, 0.14 mmol), and $Pd_2(dba)_3$ (0.065 g, 0.07 mmol). After refluxed and stirred for 4 h under an $N_2$ atmosphere, the reaction mixture was extracted with dichloromethane, washed with water, and dried over $MgSO_4$. After recrystallized by methanol and purified by column chromatography (chloroform:hexane = 5:1), the final product of **TF-ORH** was obtained as a purple solid (0.25 g, 16% yield).

$^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 7.85 (d, 0.5 Hz, 1H), 7.53 (d, $J$ = 4.0 Hz, 1H), 7.45 (s, 1H), 7.41 (d, $J$ = 4.0, 0.5 Hz, 1H), 6.93 (d, $J$ = 3.8 Hz, 1H) 6.84 (d, $J$ = 3.8 Hz, 1H), 4.12 (m, 4H), 1.71 (m, 4H), 1.27 (m, 20H), 0.88 (t, $J$ = 6.9 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$): δ (ppm) 193.99, 191.88, 167.64, 167.62, 152.39, 150.57, 138.88, 138.36, 134.94, 126.66, 124.38, 122.44, 122.11, 121.05, 116.85, 111.39, 45.18, 44.97, 31.99, 29.35, 27.24, 27.20, 27.00, 22.85, 14.31.

Anal. Calc. for $C_{32}H_{40}N_2O_3S_5$: C, 58.15; H, 6.10; N, 4.24; S, 24.26. Found: C, 55.96; H, 5.88; N, 4.30; S, 23.88.



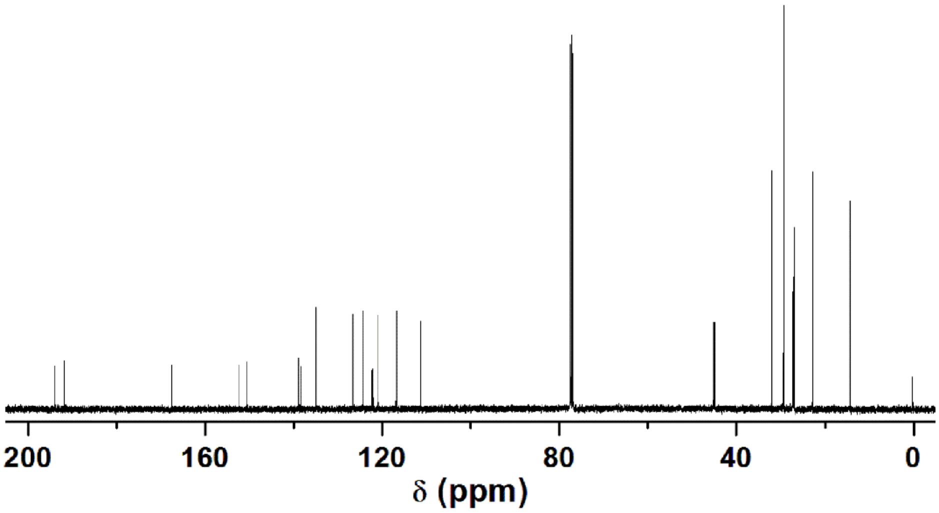


**Figure S2.** $^{1}$H (top) and $^{13}$C (bottom) NMR spectra of the **TF-ORH**.

## 2. Physical Measurements

$^1$H NMR spectra were recorded on a Bruker AVANCE III HD400 (Bruker, Germany). $^{13}$C NMR spectrum was analyzed on a Bruker AVANCE III 500 (Bruker, Germany) installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University.

Elemental analysis was performed on solid samples using a Vario-Micro Cube elemental analyzer at the Korean Basic Science Institute (KBSI) Pusan Center.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a TGA/DSC 1 and a DSC 1 (Mettler-Toledo, Switzerland), respectively, under an $N_2$ atmosphere at a heating or cooling rate of 10 ℃ min$^{-1}$.

UV–vis spectra were obtained using a Lambda 20 (Perkin-Elmer, USA) diode array diode array spectrophotometer. The small molecule films used in the UV–vis measurements were prepared by spin coating from solution on a glass substrate.

The electrochemical properties of the small molecule were studied by cyclic voltammetry (CV) with a BAS 100B electrochemical analyzer (Bioanalytical Systems, USA). A three-electrode system was used and consisted of a non-aqueous reference electrode (0.1 M Ag/Ag$^+$ acetonitrile solution), a Pt working electrode, and a Pt wire as the counter electrode. The redox potentials were measured in acetonitrile with 0.1 M ($n$-$C_4H_9$)$_4$N-$PF_6$ at a scan rate of 100 mV s$^{-1}$. The films were prepared by dip-coating the small molecule solution onto the Pt working electrode, and the measurements were calibrated using the ferrocenium (Fc$^+$)/ferrocene (Fc) redox value of –4.8 eV as an external reference. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated according to the empirical relationship HOMO = $-(E_{\text{onset,ox}} - E_{1/2,\text{Fc}} + 4.8)$ eV and LUMO = $-(E_{\text{onset,red}} - E_{1/2,\text{Fc}} + 4.8)$ eV, where $E_{\text{onset,ox}}$, $\mathrm{E}_{\text{onset,red}}$, and $E_{1/2,\text{Fc}}$ are the onset potentials of oxidation and reduction, and half-wave potential of $\mathrm{Fc/Fc^+}$ couple, respectively, assuming that the energy level of Fc is 4.8 eV below the vacuum level.[S3,S4]

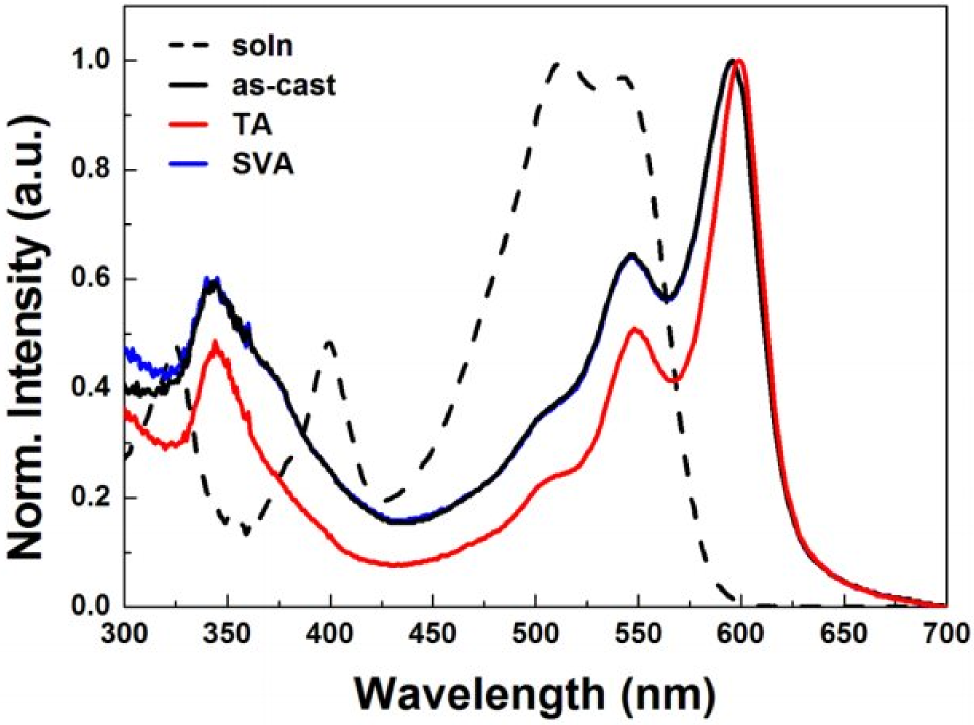


**Figure S3.** UV-vis absorption spectra of **TF-ORH** in solution and films.

## 3. Device fabrication and characterization

The device prepared in inverted structure were fabricated with the configuration ITO/ZnO NPs/PEIE/PTB7-Th:**TF-ORH**/$MoO_x$/Ag. The pre-patterned ITO-coated glass was cleaned by sequential ultrasonic treatment in detergent solution, deionized water, acetone, and isopropyl alcohol for 15 min each and subsequently dried in an oven for 5 h at 120 $^{o}$C. The ITO-coated glass substrates were pre-treated in a UV-ozone oven for 15 min. A thin sol-gel ZnO layer was spin-coated onto an ITO surface and cured at 200℃ for 60 min. The PEIE layer was deposited onto the ZnO films from the PEIE solution (in ethanol, 0.1 wt%) at 4000 rpm for 60 s. PTB7-Th and **TF-ORH** were dissolved in chloroform in a ratio of 1:2 at a total solids concentration of 15 mg $mL^{-1}$ with or without 1 vol.% diiodoctane. After filtering through a 0.45μm PTFE membrane syringe, the resulting solution was spin-coated at 4000 rpm onto the PEIE-coated substrate. The average thickness of the active layers (~100 nm) was measured with an Alpha-Step IQ surface profiler. $MoO_x$ and Ag layers were subsequently deposited onto the active layer via thermal evaporation. The active area of the device was $3 \times 3$ $mm^2$. The current density−voltage (*J*−*V*) curves were obtained using a Keithley 236 source meter with the samples in air and under AM 1.5G illumination at 100 mW $cm^{-2}$. The external quantum efficiency (EQE) was measured using a reflective microscope objective to focus the light output from a 1000 W xenon lamp outfitted with an optical chopper and a monochromator.

## 4. References

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