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Supporting Information

Ternary organic solar cells with a selenophene-containing donor guest achieve a high efficiency of 18.41%

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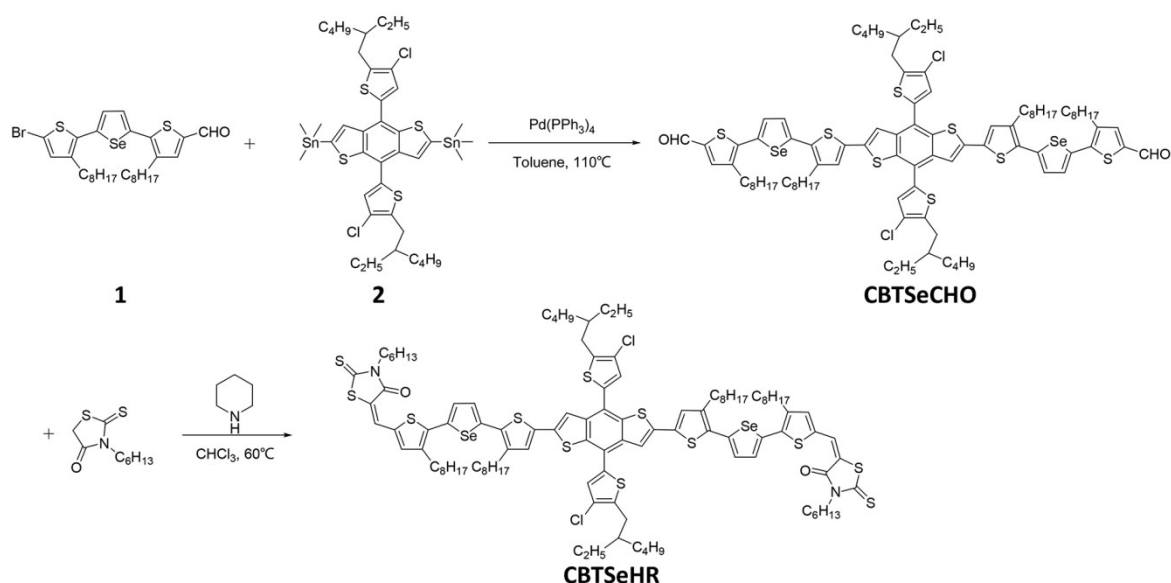
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Materials

All reactions and manipulations were carried out under nitrogen atmosphere with the use of standard Schlenk techniques. The solvents were purified and dried according to standard procedures. D18 and PNDIT-F3N were purchased from Solarmer Materials Inc. (Beijing, China). CH-6F and CBTSeHR were prepared according to the reported literature.^{1, 2} The other materials were commercially available and used without further purification.

Synthesis of CBTSeHR



Scheme S1. Synthetic routes of CBTSeHR.

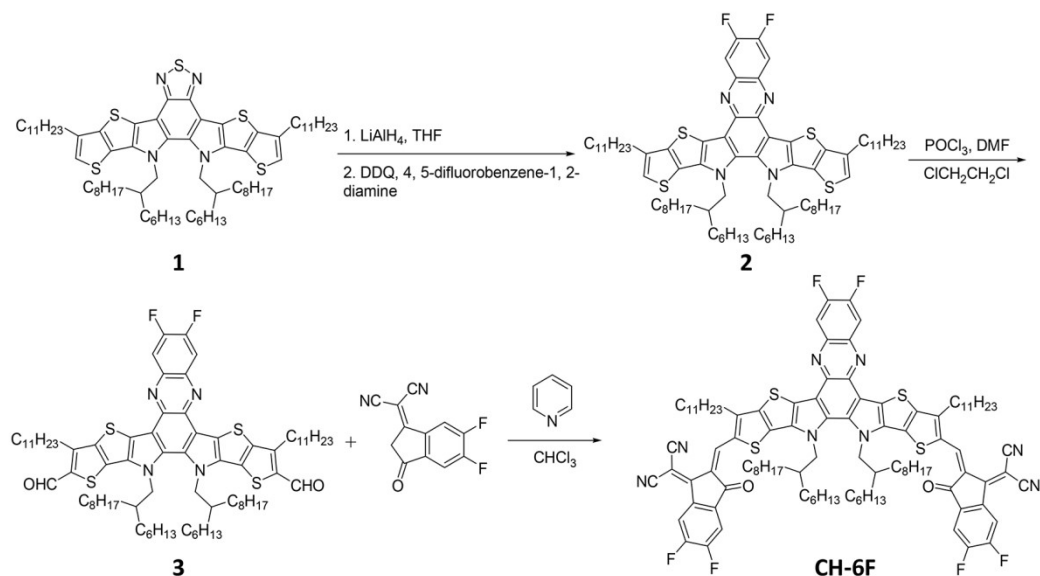
Synthesis of compound CBTSeCHO:

Under the protection of nitrogen, the weighed compound **1** (0.30 g, 0.48 mmol), compound **2** (0.22 g, 0.23 mmol) and Pd(PPh₃)₄ (20 mg) were added into the dry toluene (15 mL). Then, the reaction was stirred at 110 °C for 20 h under dark condition. After removing the solvent, the crude product was purified by silica gel chromatography using petroleum ether/dichloromethane (1:1.5, v/v) as the eluent. And the pure compound **3** was obtained as red solid (0.31 g, 78.9%).

Synthesis of **CBTSeHR**:

The compound **CBTSeCHO** (150 mg, 0.086 mmol) and 3-hexylrhodanine (187 mg, 0.86 mmol) were dissolved in dry CHCl_3 (30 mL). Then, the solution was deoxygenated by nitrogen gas for 5 min. Subsequently, dry piperidine (0.15 mL) was added by syringe and the reaction solution was heated to 60 °C. After stirring for 16 h, the mixture was poured into water (150 mL) and extracted using CHCl_3 (60 mL \times 2). The combined organic layer was washed twice with water and then dried by anhydrous Na_2SO_4 . The crude product was chromatographed by silica gel using petroleum ether/ CHCl_3 (2.5:1, v/v) as the eluent, obtaining dark purple solid (143.6 mg, 78.1%).

Synthesis of **CH-6F**



Scheme S2. Synthetic routes of **CH-6F**.

Synthesis of compound **2**:

Under the protection of nitrogen, LiAlH_4 (119 mg, 3.14 mmol) was added to a solution of compound **1** (750 mg, 0.63 mmol) in THF (50 mL). The mixture was stirred and heated to reflux for 12 h. After being cooled to 0 °C, water (30 mL) is slowly dropped into the reaction

and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was dissolved in chloroform (45 mL), then 3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 285 mg, 1.26 mmol) and 4,5-difluorobenzene-1,2-diamine (452 mg, 3.14 mmol) were added to the solution. The reaction was stirred at room temperature for 6 h, and the solvent was removed. The residue was purified by column chromatography, and the pure compound **2** was obtained as a red solid (571 mg, 71.4%).

Synthesis of compound **3**:

Under the protection of nitrogen, POCl_3 (0.3 mL) was added to a solution of compound **2** (550 mg, 0.43 mmol) and N,N-Dimethylformamide (DMF, 0.3 mL) in 1,2-dichloroethane (50 mL). After being stirred at 60 for 12 h, the resulting mixture was cooled to 0 °C and slowly added to a saturated solution of sodium acetate (40 mL), then stirred at room temperature for 2 h. The resulting mixture was extracted with dichloromethane and the organic layer was dried over anhydrous Na_2SO_4 for 1 h. After removal of solvent, the crude product was then purified by column chromatography on silica gel with petroleum ether/dichloromethane ($v/v=1:2$) as eluent to afford compound **3** as a red solid (475 mg, 82.7%).

Synthesis of compound **CH-6F**:

Under the protection of nitrogen, dry pyridine (0.2 mL) was added to a solution of compound **3** (150 mg, 0.113 mmol) and 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile (156 mg, 0.678 mmol) in CHCl_3 (25 mL). The mixture was stirred and heated to reflux for 12 h. After being cooled to room temperature, the solvent was removed.

The crude product was then purified by column chromatography on silica gel with petroleum ether/CHCl₃ (v/v=1:2) as eluent to afford **CH-6F** as a black solid (173 mg, 87%).

Measurements and Instruments

The UV-*vis* spectra of three materials in film were tested on Agilent Technologies Cary 5000 spectrophotometer. The current density-voltage (*J-V*) characteristics of all the devices were measured with a Keithley 2400 source-measure unit. Using a SAN-EI XES-70S1 AAA class solar simulator, photocurrent was performed under illumination with simulated 100 mW cm⁻² AM 1.5G irradiation. The external quantum efficiency (EQE) curve was obtained by a QE-R Solar Cell Spectral Response Measurement System.

Space charge limited current (SCLC) mobility was performed by a diode configuration of ITO/ZnO/active layer/Ag for electron mobility and ITO/PEDOT:PSS/active layer/Ag for hole mobility, respectively. The results were fitted via a space charge limited form, being described as the equation:

$$J = \frac{9\varepsilon_0\varepsilon_r\mu_0V^2}{8L^3} \exp\left(0.89\beta\sqrt{\frac{V}{L}}\right)$$

where *J* is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), ε_r is the relative dielectric constant of the transport medium, μ_0 is the hole or electron mobility, *V* (= *V*_{appl} - *V*_{bi}) is the internal voltage in the device, where *V*_{appl} is the applied voltage to the device and *V*_{bi} is the built-in voltage due to the relative work function difference of the two electrodes, *L* is the film thickness of the active layer.

Atomic force microscope (AFM) images were obtained on a Bruker MultiMode 8 in tapping mode. A FEI Tecnai G2 Spirit TWIN transmission electron microscope was used to obtain the transmission electron microscopy (TEM) images.

GIWAXS measurement was conducted at the beamline of 7.3.3 at the Advanced Light Source (ALS), and the samples were prepared on Si/PEDOT:PSS substrates under the same conditions as those used for device fabrication.

Fabrication of OSC devices

The binary and ternary devices were fabricated using a conventional structure of ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag as the following procedures. The ITO-coated glasses were cleaned using a detergent scrub, and subsequently subjected to ultrasonic treatment in soap water, deionized water, acetone and isopropyl alcohol for 15 min in each step. After drying by a nitrogen flow, the ITO substrates were treated by ultraviolet-ozone for 15 min and spin-coated with PEDOT:PSS solution at 4500 rpm for 20 s. Subsequently, the glasses were baked at 150 °C for 20 min under ambient conditions, and transferred into the glove box with nitrogen gas. Chloroform solution with D18 (4.0 mg/mL):CH-6F (1.0:1.35, w/w) for the host binary device, and D18 (4.0 mg/mL):CBTSeHR:CH-6F (1.0:0.2:1.35, w/w/w) for the ternary devices were spin-coated on the PEDOT:PSS at 2600 rpm for 30 s. Afterward, PNDIT-F3N with the concentration of 1.0 mg/mL of CH₃OH containing 0.3% (v/v) glacial acetic acid was spin-coated on the active layer at 3000 rpm for 20 s. Finally, under the high vacuum, a cathode material Ag was deposited for 150 nm onto PNDIT-F3N layer. The work area of each device is 0.04 cm², defined by the masks for all the solar cell devices discussed in this work.

Table S1 Photovoltaic performances of the as cast devices based on D18 (D₁):CBTSeHR (D₂):CH-6F (A) with different weight ratios.

D ₁ :D ₂ :A (w/w/w)	Treatment	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
1:0:1.35	As cast	0.895	24.68	0.723	15.97
1.2:0:1.35	As cast	0.897	25.06	0.702	15.78
1:0.1:1.35	As cast	0.909	24.89	0.731	16.54
1:0.2:1.35	As cast	0.916	25.26	0.748	17.33
1:0.3:1.35	As cast	0.922	25.31	0.734	17.13

Table S2 Photovoltaic performances of the optimized devices based on D18 (D₁):CBTSeHR (D₂):CH-6F (A) with different weight ratios.

D ₁ :D ₂ :A (w/w/w)	Treatment	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
1:0:1.35	TA(90°C)	0.888	26.13	0.736	17.08
1.2:0:1.35	TA(90°C)	0.884	25.69	0.724	16.44
1:0.1:1.35	TA(90°C)	0.896	26.53	0.748	17.78
1:0.2:1.35	TA(90°C)	0.901	26.64	0.767	18.41
1:0.3:1.35	TA(90°C)	0.905	26.38	0.754	18.00

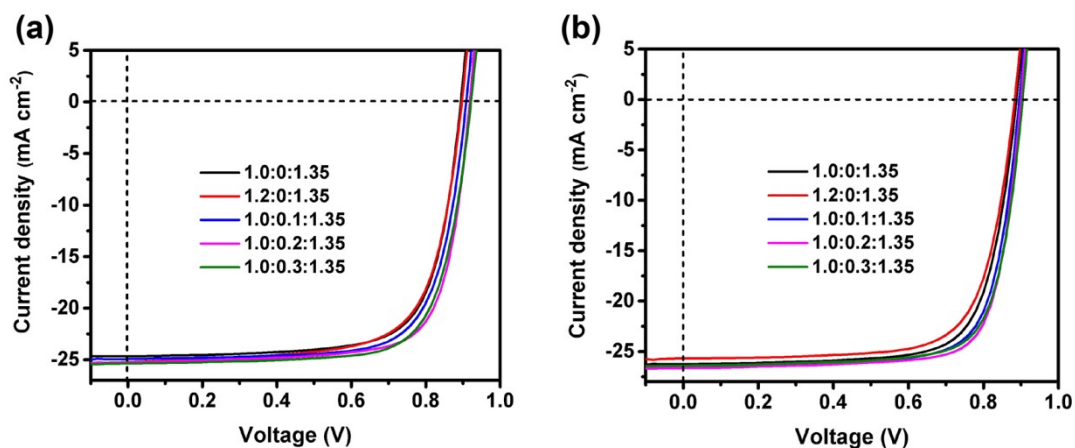


Fig. S1. Current density-voltage (J - V) curves of (a) the as cast and (b) optimized devices.

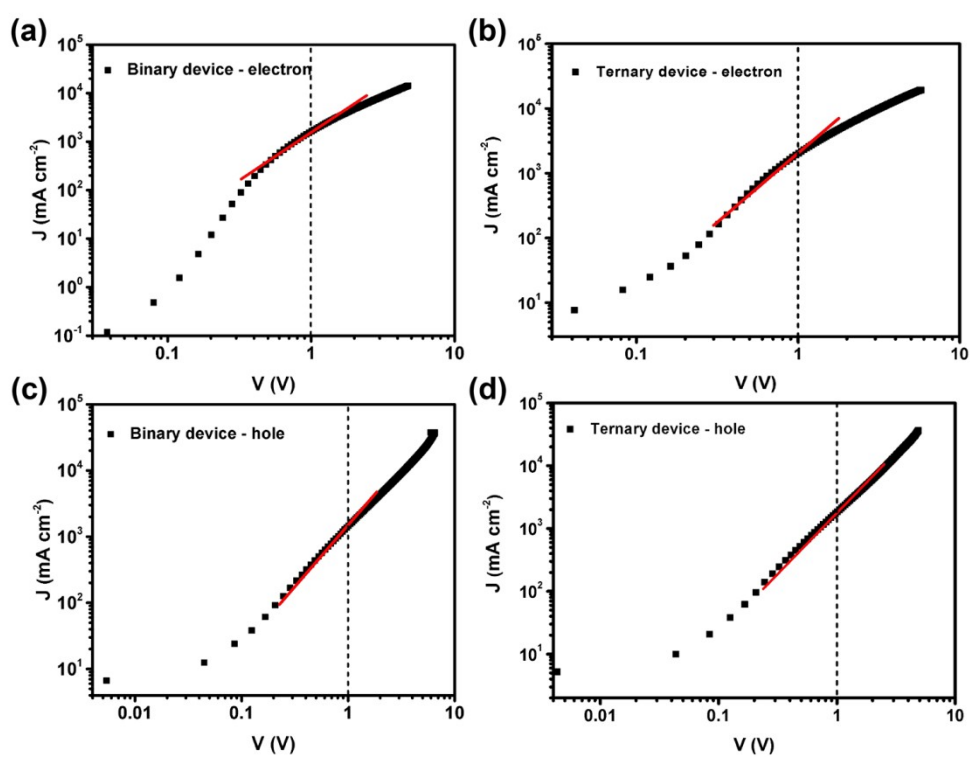


Fig. S2. The current-density-voltage (J - V) plots for electron-only devices (a, b) and hole-only devices (c, d) based on the binary and ternary blends.

References

1. H. Chen, H. Liang, Z. Guo, Y. Zhu, Z. Zhang, Z. Li, X. Cao, H. Wang, W. Feng, Y. Zou, L. Meng, X. Xu, B. Kan, C. Li, Z. Yao, X. Wan, Z. Ma and Y. Chen, *Angew. Chem. Int. Ed.*, 2022, **61**, e202209580.
2. C. Liu, Z. Wu, N. Qiu, C. Li and Y. Lu, *New J. Chem.*, 2023, **47**, 2840-2846.