Electronic Supplementary Information (ESI)

Diindeno[1,2-g:1',2'-s]rubicene: all-carbon non-fullerene electron acceptor for efficient bulk-heterojunction organic solar cells with high open-circuit voltage

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S1. Synthesis and Characterizations of DIR-2EH

2-Bromo-9,9-bis(2-ethylhexyl)-9H-fluorene (1), 9,10-bis(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-1,5-dichloro-9,10-dihydroanthracene-9,10-diol (3), 9,10-bis(9,9-bis(2-ethylhexyl)-9H-fluoren-2yl)-1,5-dichloroanthracene (4) were synthesized by pertinent procedures reported in literatures.¹, 2



Scheme S1. Synthetic routes of DIR-2EH.

Synthesis of 9,9,19,19-tetrakis(2-ethylhexyl)-9,19-dihydrodiindeno[1,2-g:1',2'-s]rubicene **DIR-2EH**:

Inside a nitrogen filled glovebox, 9,10-bis(9,9-bis(2-ethylhexyl)-9H-fluoren-2-yl)-1,5dichloroanthracene 4 (717 mg, 0.70 mmol), Pd₂dba₃ (192 mg, 0.21 mmol), P(Cy)₃ (236 mg, 0.84 mmol), DBU (7.5 mL), DMAc (18 mL) were placed in a Schlenk tube equipped with a stirring bead. The tube was sealed and then heated with stirring at 140 °C for 72 hours. After cooling, the reaction mixture was poured into methanol (100 mL). The resulting red precipitate was collected by filtration and washed with methanol. After purification by column chromatography using pure hexanes as the eluent, the product was dissolved with dichloromethane and re-precipitated with methanol (353 mg, 53%). The collected red precipitate was further purified by vacuum gradient sublimation to obtain a bright-red crystalline solid. ¹H NMR (CDCl₃, 400 MHz): δ 8.66 (d, *J* = 8.4 Hz, 2H), 8.32-8.26 (m, 4H), 8.11 (d, *J* = 6.4 Hz, 2H), 7.87-7.81 (m, 4H), 7.43-7.35 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 2H), 2.22-2.06 (m, 8H), 0.95-0.66 (m, 36H), 0.54-0.43 (m, 24H). HRMS (m/z): [M⁺] calcd for C₇₂H₈₆ 950.6730; found 956.6734. Anal. Found (Calcd): C, 90.77 (90.89); H, 9.23 (9.11).

S2. Cyclic Voltammetry (CV) Measurement.

The redox potentials of DIR-2EH and $PC_{61}BM$ were determined by cyclic voltammetry (CV) using a BAS 100B electrochemical analyzer with a scanning rate at 100 mV/s. The compounds of interest were dissolved in deoxygenated dry CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate (TBAPF₆) as the electrolyte. We used platinum working electrode and a saturated

non-aqueous $Ag/AgNO_3$ referenced electrode for the measurement. Ferrocene was used for potential calibration (all reported potentials are referenced against Ag/Ag^+). The energy level of ferrocene (4.8 eV below the vacuum level) was used as the reference.³

S3. Photoluminescence (PL) Quenching Experiment.

Photoluminescence (PL) spectra of the PL quenching experiment were recorded on a Hitachi fluorescence spectrophotometer F-4500. The quenching efficiency of DIR-2EH acceptor to P3HT donor was investigated by the Stern-Volmer equation: $I^0/I = 1 + K_{sv} \times [Q]$, where I^0 and Iis the fluorescence intensity of P3HT in the absence and presence of the quencher DIR-2EH, respectively; K_{sv} is the Stern-Volmer quenching constant, and [Q] is the concentration of DIR-2EH in chloroform. The quenching constant (K_{SV}) was estimated to be 2.5×10⁴ M⁻¹ in this experiment.



Fig. S1 PL quenching spectra of P3HT and P3HT:DIR-2EH with increasing concentration of DIR-2EH in chloroform. (left); The Stern-Volmer quenching plot for the data from P3HT:DIR-2EH.

S4. Photovoltaic Device Fabrication and Characterization.

Photovoltaic devices were fabricated on patterned ITO glass substrate. The active layer of each solar cell device is 0.10 cm². ITO glass substrates were sonicated sequentially in detergent, DI water, acetone, and isopropanol. The ITO substrates were then baked on the hot plate at 150

°C for 10 minutes. A poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) thin film was spin-coated (4000 rpm, 60 s) and then baked at 150 °C for 15 minutes. The substrate was then transferred to the nitrogen filled glove box. Next, the active layer was spin coated on top of the PEDOT:PSS layer from a 1,2-dichlorobenzene (1,2-DCB) solution of the P3HT:DIR-2EH blends with donor/acceptor ratio of 1:1, 1;2, or 1:4. The concentration of the active layer solution is 17.5 mg P3HT in 1mL 1,2-DCB. After spin coating, the active layer was slow dried inside a covered Petri dish for 60 minutes and then thermal annealed at 150 °C for 10 minutes. Finally, 20 nm of Ca and 100 nm of Al were deposited on the top of the active layer in a vacuum of about 8 \times 10⁻⁶ torr to complete the photovoltaic device fabrication. All devices were encapsulated inside a nitrogen-filled glove box.

The current density–voltage (J–V) characteristics of photovoltaic devices were measured in the dark and under AM 1.5G solar illumination from a class A solar simulator (Oriel 300W), controlled by a programmable source meter (Keithley 2400). The light intensity was calibrated using a Si photodiode (PVM 172; area = 3.981 cm2) from Nation Renewable Energy Laboratory. For the incident photon-to-electron conversion efficiency (IPCE) measurement, an AM 1.5G solar simulator was used to generate the bias light. A monochromator (Newport Model 74100), which was calibrated with a National Institute of Standards and Technology calibrated photodiode and chopped at 250 Hz, was used to select the wavelengths between 400–750 nm for illuminating the photovoltaic device. The photocurrent from the OPV was measured through the lock-in amplifier (Signal Recovery 7265), which was in turn referenced to the chopper frequency. All electrical measurements were carried out in air.

S5. Measurements of the electron mobility by the space charge limited current (SCLC) method.⁴

The devices were fabricated with an electron-only device configuration of ITO/ZnO/P3HT:PC₆₁BM (1:1) or P3HT:DIR-2EH (1:1 and 1:4)/Ca/Al. The active layers were fabricated under the condition that affords the best photovoltaic performance. The following equation was applied to estimate the electron mobility: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$ where J is the space-charge limited current, ε_0 is the permittivity of the vacuum, ε_r is the dielectric constant of the blend film, μ is the carrier mobility, and L is the active layer thickness. The bias V is corrected

for built-in voltage ($V = V_{appl} - V_{bi}$), V_{bi} , arising from the difference in the work function of the anode and the cathode. The *J*-*V* characteristics of the electron-only devices were measured under dark and are shown in Fig. S2. Electron mobilities calculated using the respective *J*-*V* curves and parameters yields $\mu_e = 6.89 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, $1.26 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, $1.99 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the blend films of P3HT:DIR-2EH = 1:1 and 1:4, and P3HT:PC₆₁BM (1:1), respectively. The electron mobility of P3HT:PC₆₁BM obtained according to our measurement is in close agreement with literature data.⁵





Fig. S2 *J-V* characteristics under dark for electron-only devices consisting of P3HT:PC₆₁BM (1:1) and P3HT:DIR-2EH (1:1 and 1:4) blend films. The solid lines represent the fitting curves.

References

- 1. J. Jo, C. Chi, S. Höger, G. Wegner, and D. Y. Yoon, Chem. Eur. J., 2004, 10, 2681.
- M. Bown, C. J. Dunn, C. M. Forsyth, P. Kemppinen, T. B. Singh, M. A. Skidmore, and K. N. Winzenberg, *Aust. J. Chem.*, 2012, 65, 145.
- 3. Y. Liu, M. S. Liu and A. K.-Y. Jen, Acta Polym. 1999, 50, 105.
- V. D. Mihailetchi, H. X. Xie, B. de Boer, L. J. A. Koster, and P. W. M. Blom, *Adv. Funct. Mater.*, 2006, 16, 699.
- 5. V. Shrotriya, Y. Yao, G. Li, and Y. Yang, Appl. Phys. Lett., 2006, 89, 063505.