Electronic Supplementary Information for:

**Developing High-Performance Small Molecule Organic Solar Cells via a Large Planar Structure and Electron-Withdrawing Central Unit**

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1. Measurements and instruments.

The $^1$H and $^{13}$C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were tested on a Bruker Autoflex III instrument. The thermogravimetric analyses (TGA) were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with 10 °C min$^{-1}$ heating rate. UV-vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with LK2010 Microcomputer-based Electrochemical Analyzer in dichloromethane solutions. All CV measurements were tested at room temperature with conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydrdide under dry argon immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s$^{-1}$. Atomic force microscopy (AFM) was performed using Multimode 8 atomic force microscope in tapping mode. The transmission electron microscopy (TEM) investigation was performed on Philips Technical G2F20 at 200 kV. The specimen for TEM measurement was prepared by spin casting the blend solution on ITO/PEDOT:PSS substrate, then floating the film on a water surface, and transferring to TEM grids.

SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/donor:acceptor/Au of hole mobility and ITO/AI/donor:acceptor/AI for electron mobility and fitting the results to a space charge limited form, where SCLC is described by

$$J = \frac{9 \epsilon_0 \epsilon_r \mu_0 V^2}{8 L^3},$$

where $J$ is the current density, $L$ is the film thickness of the active layer, $\mu_0$ is the mobility, $\epsilon_r$ is the relative dielectric constant of the transport medium, $\epsilon_0$ is the permittivity of free space (8.85 x 10$^{-12}$ F m$^{-1}$), and $V (= V_{appl} - V_{bi})$ 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 electrodes.

2. Solar cell fabrication and testing.

The devices were fabricated with a structure of glass/ITO/PEDOT:PSS/donor:acceptor/PrC60MA/AI. The ITO-coated glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultra-sonication for 15 minutes each and subsequently dried by a nitrogen flow. A thin layer of PEDOT:PSS (Baytron PVP AI 4083, filtered at 0.45 μm) was spin-coated (3000 rpm, ca.40 nm thick) onto the ITO surface. After being baked at 150 °C for 20 min, the substrates were transferred into an argon filled glove box. Subsequently, the active layer was spin-coated from blend chloroform solutions with weight ratio of DR3TBDD and PC$_{71}$BM at 1:0.8 and then annealed at 100 °C for 10 min. After cooling to the room temperature, the substrates were placed in a glass petri dish containing 1 ml chloroform for 1 minute for solvent vapor annealing (SVA). And PrC60MA solution (0.5 mg/ml, dissolved
in methanol) was spin-coated at 3000 rpm. Finally, 80 nm Al layer was deposited under high vacuum (< 1.5 x 10^-4 Pa). The effective area of each cell was 4 mm² as defined by shadow masks. The current density-voltage (J-V) characteristics of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under a simulated illumination of 100 mW cm⁻² AM1.5G irradiation using a xenon-lamp-based solar simulator [SAN-EI XES-70S1 (AM1.5G), calibrated with a standard Si solar cell.] in an argon-filled glovebox. External quantum efficiency values (EQEs) of the encapsulated devices were obtained with a halogen tungsten lamp, monochromator, optical chopper, and lock-in amplifier in air and the photon flux was determined by using a calibrated silicon photodiode.

3. Materials and synthesis.

All starting materials were purchased from commercial suppliers and used without further purification.

![Figure S1. Synthesis route of DR3TBDD.](image)

**Synthesis of compound D3TBDD**

A solution of Sn-3T2S (4.0 g, 5.24 mmol) and BDD (1.2 g, 2.00 mmol) in toluene (50 ml) was degassed twice with argon, after which Pd(PPh₃)₄ (50 mg, 0.043 mmol) was added and the mixture was stirred as 100 °C for 24 h under argon. Then the mixture was poured into water (100 ml), and extracted with chloroform. The organic layer was washed with water, and then dried over anhydrous Na₂SO₄. The solvent was removed by a rotating evaporator and the residue was purified by silica gel chromatography using a mixture of petroleum ether and dichloromethane (2:1) eluent to produce compound D3TBDD (1.95 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ 7.72 (s, 2H), 7.25 (d, J=3.6 Hz,2H), 7.22-7.21 (d, J=5.2 Hz, 2H), 7.15-7.14 (d, J=3.6 Hz, 2H), 7.01-6.99 (d, J=5.2 Hz, 2H), 3.36-3.35 (m, 4H), 2.92-2.86 (m, 8H), 1.91-1.89 (m, 2H), 1.88-1.71 (m, 8H), 1.45-1.40 (m, 56H), 1.12-1.08 (m, 6H), 1.05-1.01 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): 177.16, 152.49, 141.84, 139.56, 139.23, 136.81, 135.60, 135.30, 133.57, 133.01, 131.80, 131.29, 130.63, 130.14, 126.24, 125.91, 123.71, 41.06, 33.08, 32.11, 30.88, 29.73, 28.96, 28.00, 26.97, 23.25, 22.90, 17.51, 14.29, 11.05. MS (MALDI-TOF): calcd for C₸₂H₁₁₂O₂S₈ [M⁺],1384.64; Found: 1385.67.

**Synthesis of compound DCHO3TBDD**
A Vilsmeier reagent, which was prepared with POCl₃ (0.46 ml, 5.00 mmol) in DMF (10 ml), was added to a solution of D3TBDD (1.38g, 1.0 mmol) in 1,2-dichloroethane (80 ml) at 0 °C. After being stirred at 90 °C for 12 h, the mixture was poured into ice water (300 ml), neutralized with Na₂CO₃, and then extracted with chloroform. The combined organic layer was washed with water and brine, dried over Na₂SO₄. After removal of solvent it was chromatographed on silica gel using a mixture of dichloromethane and petroleum ether (2:1) as eluent to afford DCHO3TBDD (1.1 g, 76%). ¹H NMR (400 MHz, CDCl₃): δ 9.95 (s, 2H), 7.73-7.55 (m, 4H), 7.28-7.25 (m, 4H), 3.34-3.30 (m, 4H), 2.87-2.81 (m, 8H), 1.80 (s, 2H), 1.73 (s, 6H), 1.44-1.28 (m, 56H), 1.00-0.97 (m, 6H), 0.95-0.90 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 183.00, 178.03, 153.83, 142.41, 141.63, 141.02, 140.74, 139.60, 138.50, 135.88, 135.09, 134.28, 133.58, 132.90, 132.49, 131.53, 129.49, 128.44, 127.27, 41.85, 39.48, 34.36, 33.61, 32.63, 32.63, 32.25, 30.97, 30.41, 29.55, 26.85, 23.75, 23.39, 14.81, 11.63. MS (MALDI-TOF): calcd for C₉₄H₁₁₂O₃S₈ [M⁺], 1440.63; Found: 1441.89.

Synthesis of compound DR3TBDD

DCHO3TBDD (300 mg, 0.21 mmol) and 3-ethylrhodanine (336 mg, 2.1 mmol) was dissolved in a dry CHCl₃ (50 ml) solution, and then 1 ml piperidine was added to the mixture under the protection of argon, and stirring at room temperature for 24 h. Then, the mixture was poured into water (200 ml), and extracted with CHCl₃. The organic layer was washed with water, and then dried over Na₂SO₄, and evaporated. The crude product was purified by silica gel using chloroform as eluent and then recrystallized from hexane and CHCl₃ mixture to afford DR3TBDD as dark solid (200 mg, 55%). ¹H NMR (400 MHz, CDCl₃): δ 7.78 (s, 2H), 7.66 (s, 2H), 7.29-7.24 (m, 6H), 4.24-4.18 (m, 4H), 3.41-3.28 (m, 4H), 2.86-2.83 (m, 8H), 1.83-1.80 (m, 2H), 1.78-1.68 (m, 8H), 1.47-1.28 (m, 56H), 1.02-0.99 (m, 6H), 0.94-0.89 (m, 18H). ¹³C NMR (100 MHz, CDCl₃): δ 192.00, 177.50, 167.27, 153.30, 141.77, 141.10, 140.04, 139.50, 137.40, 137.32, 135.23, 134.51, 133.68, 132.91, 132.25, 131.68, 127.27, 126.69, 124.84, 120.58, 41.15, 39.92, 33.67, 32.87, 31.94, 30.56, 30.27, 29.72, 29.63, 29.53, 29.48, 29.36, 29.31, 28.84, 26.12, 23.06, 22.71, 14.15, 12.31, 10.96. MS (MALDI-TOF): calcd for C₉₄H₁₂₂N₂O₁₃S₁₂ [M⁺], 1726.61; Found: 1727.64.

Figure S2. TGA curve of DR3TBDD with a heating rate of 10 °C/min under N₂ atmosphere.
**Figure S3.** Cyclic voltammogram of ferrocene/ferrocenium in a dichloromethane solution of 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$ with a scan rate of 100 mV s$^{-1}$.

**Figure S4.** The frontier molecular orbital surfaces of DR3TBDD.

**Figure S5.** The chemical structure of PrC60MA.
Figure S6. $^1$H NMR spectra of compound D3TBDD and the aromatic region at 300K in CDCl$_3$. 
Figure S7. $^{13}$C NMR spectra of compound D3TBDD at 300K in CDCl$_3$. 
Figure S8. $^1$H NMR spectra of compound DCHO3TBDD and the aromatic region at 300K in CDCl$_3$. 
Figure S9. $^{13}$C NMR spectra of compound DCHO3TBDD at 300K in CDCl$_3$. 
Figure S10. $^1$H NMR spectra of compound DR3TBDD and the aromatic region at 300K in CDCl$_3$. 
**Figure S11.** $^{13}$C NMR spectra of compound DR3TBDD at 300K in CDCl$_3$. 

![13C NMR spectra of compound DR3TBDD at 300K in CDCl3.](image)
Figure S12. MALDI-TOF plot of compound D3TBDD.

Figure S13. MALDI-TOF plot of compound DCHO3TBDD.
Figure S14. MALDI-TOF plot of compound DR3TBDD.